PB-213 841

TREATMENT OF WASTEWATER FROM THE PRODUCTION OF POLYHYDRIC ORGANICS

M. A. Zeitoun, et al

Dow Chemical Company
Freeport, Texas

October 1971

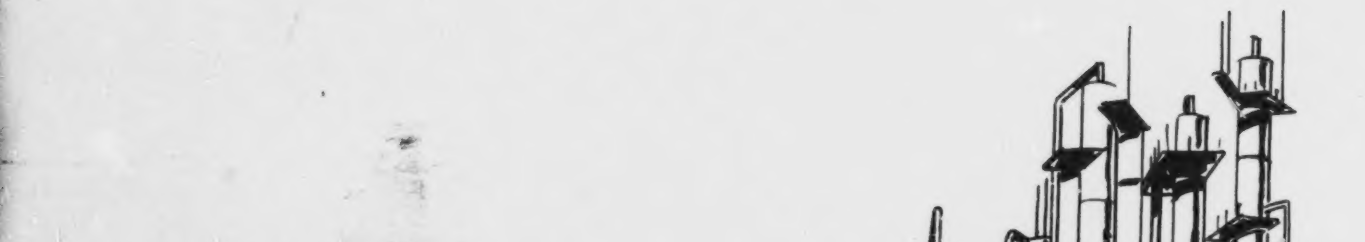
DISTRIBUTED BY:

NTIS
National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

CLEAN WATER WATER POLLUTION CONTROL RESEARCH SERIES ● 12020 EEQ 10/71

PB 213 841

Treatment of Wastewater From The Production of Polyhydric Organics



Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

U.S. ENVIRONMENTAL PROTECTION AGENCY

207

WATER POLLUTION CONTROL RESEARCH SERIES

The Water Pollution Control Research Series describes the results and progress in the control and abatement of pollution in our Nation's waters. They provide a central source of information on the research, development, and demonstration activities in the Environmental Protection Agency, through inhouse research and grants and contracts with Federal, State, and local agencies, research institutions, and industrial organizations.

Inquiries pertaining to Water Pollution Control Research Reports should be directed to the Chief, Publications Branch, Research Information Division, Research and Monitoring, Environmental Protection Agency, Washington, D. C. 20460.

TREATMENT OF WASTEWATER FROM THE PRODUCTION OF POLYHYDRIC ORGANICS

by

The Dow Chemical Company
Texas Division
Freeport, Texas 77541

for the

OFFICE OF RESEARCH AND MONITORING

ENVIRONMENTAL PROTECTION AGENCY

Project No. 12020-EEQ

October, 1971

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402 - Price $1.75

EPA Review Notice

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

A number of extremely useful and widely produced compounds are produced by the alkaline hydrolysis of chlorohydrins. Ethylene and propylene glycols and glycerin are produced in this manner.

The brine wastewater resulting from the production of the glycols is characterized by a high salt content (8-10% NaCl), excess alkalinity, and the presence of several organic compounds.

Several processes were examined in the laboratory to determine the usefulness for the treatment of the brine wastewater.

Solvent extraction of the glycol wastewater with secondary or tertiary amines produces a raffinate that is salt-saturated and low in glycol and a product enriched in the glycol and nearly free of salt. The required large solvent-to-feed ratio, the requirement for near-freezing temperatures, and the high reflux to produce a pure product, make solvent extraction, as a treatment method, uneconomical.

Adsorption of glycols on activated carbon was found to be unfeasible because of the low capacity of carbon for the glycols. Commercially available cellulose acetate membranes with low salt rejection were found to exhibit a high pore flow of propylene glycol and were therefore unable to significantly separate the salt and the glycol.

Biological oxidation of propylene glycol wastewater in batch and continuous laboratory units gave a total oxygen demand (TOD) removal efficiency of 86 to 88% at a residence time of 12 hours.

An activated sludge pilot plant with a feed rate of 0.5 gpm was constructed and successfully operated as a completely mixed aerator on an equalized propylene glycol wastewater. Removal efficiencies of over 90% at a retention time of 8.0 hours at loadings of 2.0 to 3.0 pounds total oxygen demand (TOD) per pound of mixed liquor volatile suspended solids (MLVSS) per day were obtained. The effluent quality was improved by operation at recycle ratios of 24 to 40%.

The operational and design parameters determined from the pilot plant operation were used to design an activated sludge plant to treat 6 MGD of wastewater resulting from the production of 1.2 million pounds per day of propylene glycol at an estimated operating cost of 3.3 cents per pound of TOD removed or less than 0.2 cent per pound of propylene glycol produced. The total fixed captial requirement for a 6-MGD plant was estimated to be 1.4 million dollars.

TABLE OF CONTENTS

Section Page

I. Conclusions 1

II. Recommendations 5

III. Introduction 7

IV. Characterization of the Wastewaters 11

V. Renovation and Purification Processes 25

- A. Solvent Extraction With Secondary and Tertiary Amines 25
- B. Carbon Adsorption 37
- C. Membrane Separations 46

VI. Biological Treatment 49

- A. Biodegradability of Glycols in Saline Waters 49
- B. Treatability Studies 50
- C. Batch Kinetics 56
- D. Bench Scale Continuous Units 66

VII. Activated Sludge Pilot Plant 71

- A. Plant Description and Operation 71
- B. Evaluation of the Roughing Column 78
- C. Results of Different Modes of Operation 80
- D. Operational and Design Parameters 86
- E. Polishing of the Biotreatment Plant Effluent With Activated Carbon 111

VIII. Conceptual Design of a 6-MGD Activated Sludge Waste Treatment Plant 115

- A. Process Description and Plant Design 115
- B. Cost Estimate and Economic Evaluation 125

IX. Acknowledgments 133

X. References 135

XI. Appendices 137

LIST OF FIGURES

Number		Page
III-1	Production of Propylene Glycol by the Chlorohydrin Process	8
IV-1	Biological Oxidation of Ethylene and Propylene Glycols	20
IV-2	Biological Oxidation of Ethylene and Propylene Oxides	21
IV-3	Biological Oxidation of Organic Components of the Ethylene Glycol Waste (Acclimated Seed)	23
V-1	Schematic Diagram of the Solvent Extraction Process	27
V-2	Solubility Diagram - Di-isopropylamine Water NaCl System	28
V-3	Phase Diagram of Extraction Results - Stage Calculation for Sodium Chloride (Solvent - Methyl Diethyl Amine)	35
V-4	Adsorption of Glycols on Witco Carbon 20 x 40 Mesh	38
V-5	Effect of pH on Uptake of Propylene Glycol by Witco Carbon 20-40 Mesh (C_o = 2000 ppm)	39
V-6	Fixed Bed Adsorption of Propylene Glycol on Witco Carbon	42
V-7	Fixed Bed Adsorption of Ethylene Glycol on Activated Carbon	43
VI-1	Biotreatability Tests, Loading-Removal Curve for Propylene Glycol Waste (NaCl 9-10.5%) (Acclimated Mixed Culture)	52
VI-2	Biotreatability Tests, Effluent-Loading Curve for Propylene Glycol Waste (Acclimated Mixed Culture)	53
VI-3	Biotreatability Tests, Loading-Removal Curves - Propylene and Ethylene Glycol Wastes (Bacterium No. 52)	54

List of Figures (Cont'd)

Number		Page
VI-4	Biotreatability Tests, Effluent-Loading Curve for Propylene Glycol Waste (Bacterium No. 52)	55
VI-5	Batch Kinetics, Propylene Glycol - 10% NaCl, Acclimated Mixed Culture	57
VI-6	Batch Kinetics, Propylene Glycol - 10% NaCl, Acclimated Mixed Culture	58
VI-7	Batch Kinetics, Propylene Glycol Wastewater, Acclimated Mixed Culture	59
VI-8	Batch Kinetics, Ethylene Glycol Wastewater, Acclimated Mixed Culture	61
VI-9	Batch Kinetics, Propylene Glycol - 10% NaCl, Bacterium No. 52	62
VI-10	Biological Reaction Rate of Propylene Glycol	64
VI-11	Complete Mixing Kinetics in a Single Basin	65
VI-12	Calculated Treatment Efficiency of Propylene Glycol in a Continuous System	67
VI-13	Bench Scale Continuous Bio-oxidation Unit	68
VI-14	Loading-Removal Relationship, Bench Scale Continuous Unit (Bacterium 52 - Propylene Glycol - 8.5% Salt)	70
VII-1	Activated Sludge Miniplant - Flow Diagram	72
VII-2	Aeration Tank	74
VII-3	First Settling Tank and Composite Samplers	75
VII-4	Flocculation Vessel With pH Control	76
VII-5	Pilot Plant Operation - Mixed Propylene and Ethylene Glycols Wastewater (Plug Flow Operation)	81
VII-6	Activated Sludge Pilot Plant Operation - Plug Flow - Mixed Ethylene Glycol and Propylene Glycol Wastewater	83

List of Figures (Cont'd)

Number		Page
VII-7	Loading-Removal Curve, Plug Flow - Mixed Ethylene and Propylene Glycol Wastewater	84
VII-8	Effluent Loading Curve, Plug Flow - Mixed Ethylene and Propylene Glycol Wastewater	85
VII-9	Pilot Plant Operation - Propylene Glycol Waste, Completely Mixed Reactor	87
VII-10	Pilot Plant Operation - Equalized Propylene Glycol Waste - Completely Mixed Reactor	88
VII-11	Pilot Plant Operation - Equalized Propylene Glycol Waste	89
VII-12	Loading-Removal Curve - Equalized Propylene Glycol Wastewater	90
VII-13	Effect of Temperature on Uptake Rate	92
VII-14	Effluent-Loading Curve, Propylene Glycol Equalized Feed - Completely Mixed Aerator	94
VII-15	TOD Removal Rate as Function of Load Ratio - Propylene Glycol Equalized Feed - Completely Mixed Reactor	95
VII-16	Continuous Laboratory Unit for Oxygen Uptake Measurements	96
VII-17	Oxygen Uptake - Propylene Glycol Wastewater - 20°C	98
VII-18	Oxygen Utilization (Temperature 20° to 25°C)	99
VII-19	Effect of Aeration Rate on Oxygen Transfer	102
VII-20	Oxygen Mass Transfer (Non-Steady State Method)	103
VII-21	Gross Solids Formation	104
VII-22	Sludge Settling Paths - C_o=900 ppm., SVI=70	106
VII-23	Sludge Settling Paths - C_o=1100 ppm., SVI=53	107
VII-24	Sludge Settling Paths - C_o=1700 ppm., SVI=42	108

List of Figures (Cont'd)

Number		Page
VIII-1	Activated Sludge Plant - 6 MGD, Flow Diagram	117
VIII-2	Activated Sludge Plant - 6 MGD, Plant Layout	118
VIII-3	Activated Sludge Plant - 6 MGD, Pretreatment and Aeration	123
VIII-4	Activated Sludge Plant - 6 MGD, Details of Aeration Basin	126
VIII-5	Activated Sludge Plant - 6 MGD, Sludge Handling	127
XI-1	Precision Control Chart - TOD Analysis	143
XI-2	Precision Control Chart - Glycol VPC Analysis	144

LIST OF TABLES

Number		Page
I-1	Activated Sludge Treatment of Glycol Waste Brines - Operational and Design Parameters	4
IV-1	Ethylene System Wastewater (Composite Analyses)	12
IV-2	Propylene System Wastewater (Composite Analyses)	13
IV-3	Organics in Ethylene System Wastewater	15
IV-4	Organics in Propylene System Wastewater	16
IV-5	Biological and Chemical Oxygen Demand of Wastewater From Propylene System	18
IV-6	Correlation of Chemical and Biological Oxygen Demand - Propylene Glycol Wastewater	19
IV-7	Trace Elements in Typical Glycol Wastes	24
V-1	Equilibrium of Diisopropyl Amine-Saturated NaCl Solution - Glycol	29
V-2	Equilibrium of Methyl Diethyl Amine-Saturated NaCl Solution - Ethylene Glycol	32
V-3	Equilibrium of Methyl Diethyl Amine - 10% NaCl Solution - Ethylene Glycol	34
V-4	Fixed Bed Adsorption of Propylene Glycol on Witco Carbon	41
V-5	Fixed Bed Adsorption of Propylene Glycol on Activated Carbon	45
V-6	Evaluation of Cellulose Membranes for the Separation of Propylene Glycol and Salt	47
VI-1	Batch Kinetics of Bio-oxidation of Ethylene and Propylene Wastewaters	63
VII-1	Operation of the Roughing Column With Forced Draft Air	79
VII-2	Carbon and Oxygen Balance of the Activated Sludge Process	110

List of Tables (Cont'd)

Number		Page
VII-3	Summary - Glycol Waste Treatment, Activated Sludge Design Parameters	112
VIII-1	Design Feed, 6 MGD Activated Sludge Wastewater Treatment Plant	116
VIII-2	Major Equipment - 6 MGD Activated Sludge Wastewater Treatment Plant	119
VIII-3	Major Instrumentation - 6 MGD Activated Sludge Wastewater Treatment Plant	121
VIII-4	6 MGD Activated Sludge Waste Treatment Plant - Estimate of Direct Capital Cost	129
VIII-5	6 MGD Activated Sludge Waste Treatment Plant - Computation of Fixed Capital	131
VIII-6	6 MGD Activated Sludge Waste Treatment Plant - Estimate of Operating Cost	132
XI-1	Determination of Suspended Solids - Comparison of Methods	141
XI-2	Pilot Plant Operation, Mixed PG and EG Wastewaters - Plug Flow Reactor	146
XI-3	Pilot Plant Operation, Propylene Glycol Waste - Completely Mixed Reactor	150
XI-4	Pilot Plant Operation, Equalized Propylene Glycol Waste - Completely Mixed Reactor	154
XI-5	Pilot Plant Operation, Equalized Propylene Glycol Waste - Completely Mixed Reactor	157
XI-6	Biochemical Test Reactions for Gram Negative Rod Bacteria From the Activated Sludge	162
XI-7	Biochemical Test Reactions for Gram Positive Bacteria From the Activated Sludge	164

SECTION I

CONCLUSIONS

The following conclusions are based on the study of several alternate processes for the treatment of the saline wastewater resulting from the production of polyhydric organic compounds by the chlorohydrin process and on the successful operation of a biological oxidation pilot plant.

The conclusions are:

1. The wastewater resulting from the production of ethylene or propylene glycol is characterized by a high salt content (8 to 10% NaCl), a pH of 11.0 to 12.0, and the presence of relatively high concentration of the glycol, (500-1000 ppm.). Other organics present in concentrations less than 100 ppm. are the oxide, the dichloride, the chlorohydrin and a chlorinated ether. A propylene glycol wastewater may also contain appreciable concentrations of acetol and acetic acid, both of which are oxidation products of propylene glycol.

2. Instrumental methods that determine total organic carbon (TOC) and the total oxygen demand (TOD) were found to be considerably more effective than biological oxygen demand (BOD), and chemical oxygen demand (COD) in the correlation of the laboratory and pilot plant data. The total oxygen demand determination and the chromotographic analysis of the organic components in solution were adopted during this study as the principal measures of the organic content of the raw and processed wastewaters.

3. Solvent extraction of the glycol wastewater with secondary or tertiary amines produces a salt saturated raffinate, low in glycol, and a product enriched in the glycol and nearly free of salt. The necessity for high reflux to produce a pure product and the cost of solvent recovery from both the raffinate and product, added to the required large solvent inventory, and the low temperature operation (0°C.) make solvent extraction uneconomical for the treatment of wastewater from glycol production.

4. Carbon adsorption is not feasible because of the low capacity of the activated carbons for the glycols that is further reduced by the competitive adsorption of the chlorinated organics present in the wastewater. Regeneration of the activated carbon with methanol in fixed bed operation produces a glycol solution free of salt, but the washing of the methanol is inefficient resulting in appreciable solvent losses.

5. Commercially available cellulose acetate membranes with low salt rejection exhibit a high pore flow of propylene glycol and thus produce no significant separation of the salt and the glycol.

6. All the organic components of glycol wastewater are biodegradable by well acclimated cultures, except the chlorinated ethers. These seem to be poisonous at high concentrations (over 100 ppm.) or in a batch system, but can be tolerated in continuous flow reactors.

7. A rather long acclimation period (6-8 weeks) is required to develop a mixed culture activated sludge that tolerates the high salt and utilizes the glycols as the only carbon source.

8. Biological oxidation of propylene glycol wastewater in batch fill and draw aerators has a reaction rate of 0.48 hour^{-1} based on the removal of the total oxygen demand (TOD). Calculated treatment efficiency in a continuous system is 86% for a residence time of 12 hours.

9. Continuous laboratory biotreatment units removed 88% of the incoming TOD from propylene glycol waste at a residence time of 12 hours. The effluent from the laboratory units was turbid and contained about 300 ppm. TOD, almost entirely metabolites and cell fragments. These could be reduced to 100-150 ppm. by chemical flocculation.

10. Tertiary treatment of the effluent from the activated sludge process, with activated carbon, produces a salt solution containing less than 10 mg./l. of organic carbon, which can be recycled as feed to the chlorine cells. The economics of carbon adsorption is not attractive due to the low capacity of the carbon and the cost of thermal regeneration.

11. The operation of a 0.5 gpm. activated sludge pilot plant (aeration volume $\simeq$ 250 gallons) as a plug flow reactor on a mixed ethylene and propylene glycol wastewaters produced an average removal efficiency of 84% at a residence time of 12 to 14 hours. An effluent quality below 200 ppm. TOD can be obtained at loadings of up to 2.0 lbs. TOD/lb. MLVSS·day.

12. The completely mixed mode of operation of the pilot plant with equalized feed is advantageous. Removal efficiencies of over 90% were obtained at retention time of 8.0 to 9.0 hours, and at loadings of 2.0 to 3.0 lbs. TOD/lb. MLVSS·day. The effluent quality is improved by operating at a recycle ratio of 25-40%, and the chemical flocculant requirements for clarification is reduced.

13. The operational and design parameters of the activated sludge process for the treatment of equalized glycol brine waste are shown in Table I-1.

14. An activated sludge plant designed for the treatment of 6 MGD of propylene glycol wastewater, resulting from the production of about 1.2 million pounds per day of the glycol, would include the following sequential steps:

a. A cooling and equalization pond.
b. Neutralization to pH below 9.0 with 38% HCl.
c. Addition of nutrients as phosphoric acid and ammonia and the addition of dilution water to replace the evaporation losses in the pond.
d. An aeration basin with the required surface aerators.
e. A clarifier and sludge recycle to the aeration basin.
f. A thickener and centrifuges to concentrate the excess sludge to 18-20% solids before transport to landfill.

The total fixed capital required is estimated at 1.4 million dollars. The total operating cost is 775,000 $/year, including the $430,000 cost of the acid required for the neutralization.

The cost per pound TOD removed is 3.23 cents, and is less than 0.2 cents per pound of propylene glycol produced.

15. As a result of this investigation, an activated sludge plant is being built by The Dow Chemical Company at Freeport, Texas, to treat up to 300 gallons per minute of propylene glycol wastewater. The plant utilizes one 50 H.P. surface aerator in the aeration basin, comprising a single, full-scale element of a larger plant.

TABLE I-1

ACTIVATED SLUDGE TREATMENT OF GLYCOL WASTE BRINES OPERATIONAL AND DESIGN PARAMETERS

Removal efficiency:	90-92%
Optimum temperature:	30-35°C.
Allowable temperature range:	17-40°C.
Nutrient requirements:	TOD:N:P = 300:10:1
Removal rate:	$\frac{TOD_i - TOD_e}{t \times TOD_e} = 1.33 - 0.42 \frac{TOD_i}{MLVSS}$
Oxygen utilization:	Lbs. O.C./day = 0.256 (Lbs. TOD removed /day) + 0.13 (lbs. MLVSS)
Oxygen transfer:	$\alpha = 1.2$ $\beta = 0.47$
Sludge production:	Lbs. VSS formed/day = 0.133 (lbs. TOD removed/day) - 0.021 (lbs. MLVSS)

The symbols used are defined in Table VII-3.

SECTION II

RECOMMENDATIONS

Based upon the operating and engineering experience gained during this investigation, the following recommendations for improving the technology of wastewater treatment in the petrochemical industries are made:

1. Particular emphasis should be given to the chemical and biological characterization of the waste streams. This includes the detection of the specific organic components in the wastewater and their biological oxidation rates.

2. Instrumental methods that determine total organic carbon (TOC) and total oxygen demand (TOD) should be substituted for the BOD_5 and COD tests, for the reliable interpretation of behavior and fate of the organics in the wastewaters and for the evaluation of treatment processes.

3. Batch biological treatability tests should be limited to a period of acclimation that may extend to several months and could be used to determine the approximate process kinetics. However, continuous pilot systems should be used to determine the design parameters of a treatment facility.

4. An equalization basin to dampen the fluctuations of the organics in the wastewater resulting from petrochemical operations is a necessity and should be provided. The basin can also act as a cooling pond if the waste stream is released at a temperature too high for proper operation of the biological treatment unit.

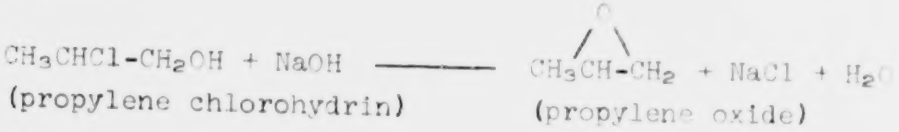
5. There is a critical need for the development of control systems so that an activated sludge process can be operated as efficiently as chemical processes. The performance of an activated sludge process is greatly improved and its reliability increased under steady state conditions. This can only be achieved by instrumentation to control the food to bacteria ratio in the aeration basin, the nitrogen and phosphorous requirement and the treatment temperature. A biological toxin detector to detect and eliminate a toxic substance before it can enter the aeration basin is greatly needed.

SECTION III

INTRODUCTION

A number of extremely useful and widely produced chemicals are manufactured by the alkaline hydrolysis of chlorohydrins. Both ethylene and propylene glycols as well as glycerin are produced in this manner.

A flow sheet of the chlorohydrin process for the production of polyhydric compounds, exemplified by propylene glycol is shown in Figure III-1. The caustic hydrolysis of the chlorohydrin to the oxide takes place in the aqueous phase and a molecule of sodium chloride is produced for each molecule of oxide formed:



$$CH_3CHCl-CH_2OH + NaOH \longrightarrow CH_3\overset{O}{CH-CH_2} + NaCl + H_2O$$

(propylene chlorohydrin) (propylene oxide)

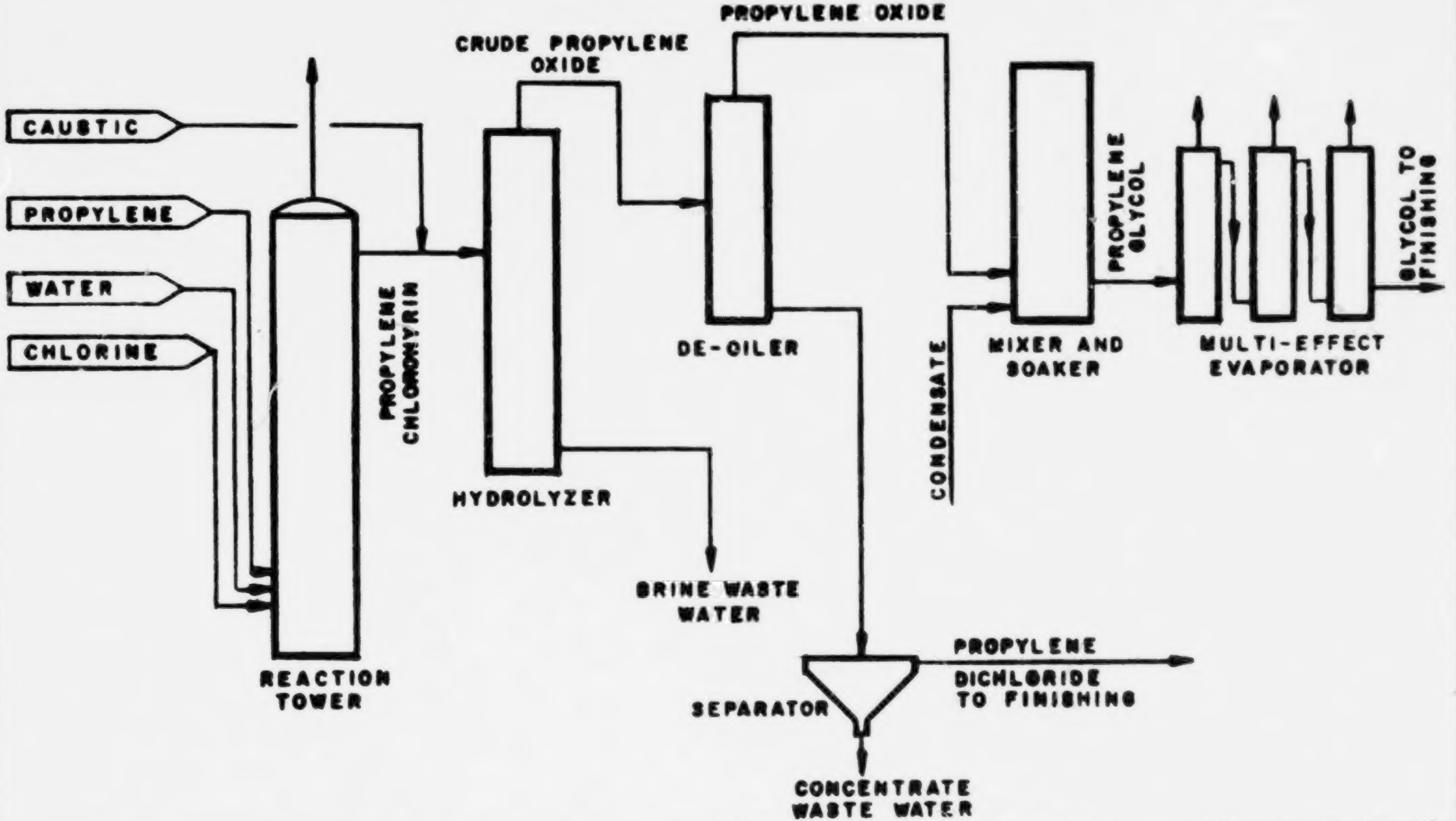
The hydrolyzer is a separation column in which the overhead product is the oxide and the bottoms contain the unreacted chlorohydrin, any excess caustic, the produced sodium chloride, and several organic materials at low concentrations. The largest in concentration is the glycol which results from the overlap in the rates of the several reactions.

A typical propylene glycol plant produces about 5.4 gallons of wastewater for each pound of propylene glycol. The large amount of the wastewater and its high salinity make this a particularly difficult waste to handle by conventional techniques.

The overall objective of this program, under the grant from the Environmental Protection Agency, was to systematically characterize the physical, chemical, and biological nature of the brine waste resulting from the production of polyhydric organic compounds and to develop a method of treatment. More specifically, the objective was to examine several alternate treatment methods and to determine the technical, engineering, and economic feasibility of each. The processes to be examined were:

1. Biological Treatment - The objective was to develop a biological oxidation process that would require a minimum of dilution of the brine waste or that exhibited a maximum tolerance of salinity at high purification rates. The microbial metabolism of ethylene and propylene glycols in the presence of sodium chloride was the subject of a subcontract

FIGURE III - I
PRODUCTION OF PROPYLENE GLYCOL BY THE CHLOROHYDRIN PROCESS


CAUSTIC
PROPYLENE
WATER
CHLORINE
REACTION TOWER
PROPYLENE CHLOROHYRIN
CRUDE PROPYLENE OXIDE
HYDROLYZER
BRINE WASTE WATER
PROPYLENE OXIDE
DE-OILER
SEPARATOR
CONCENTRATE WASTE WATER
PROPYLENE DICHLORIDE TO FINISHING
CONDENSATE
MIXER AND SOAKER
PROPYLENE GLYCOL
MULTI-EFFECT EVAPORATOR
GLYCOL TO FINISHING

by the Texas A. and M. Research Foundation. Organisms were to be sought in areas exposed to glycol and glycerin wastes, from hyper-saline soils, from known cultures, and from other saline sources including seawater and naturally saline lakes and enclosed bays.

2. Solvent Extraction With Secondary and Tertiary Amines - The solvent extraction process as developed for the reclamation of saline water, if applicable to the glycol wastewater, could enable recovery of the glycol in a relatively pure water product. The raffinate would be a saturated salt solution low in organics that could be used as feed to chlorine cells for the production of the caustic required in the hydrolysis. This would then represent a completely closed cycle with no waste to be discharged.

3. Adsorption and Recovery of the Glycol - The adsorptive capacity of activated charcoal for ethylene and propylene glycols was known to be low, but investigations of several regeneration methods that would result in the recovery of the glycol as a product were part of this program. The use of activated carbon as a pretreatment for an activated sludge process, or as a tertiary treatment to polish the biologically treated waste were also to be investigated.

4. Membrane Separation - Many potential chemical and physical processes for the removal and recovery of glycols from the hydrolyzer effluent are inoperable because of the presence of the large amounts of salt. Membranes that would allow selective separation of the salt and the glycol would allow these other processes to be employed. The screening of potential membranes highly permeable to NaCl but rejecting propylene glycol was done by the Gulf South Research Institute in New Orleans, Louisiana, as a part of a separate R. and D. grant (Project No. 12020DQC) awarded to the State of Louisiana Department of Commerce and Industry by the Environmental Protection Agency.

The final objective was to develop sufficient pilot plant information, based on the most economically attractive of the processes examined, for the conceptual design of a waste treatment facility. Hopefully, the process developed and engineered would then be applicable to other organically contaminated waste brines.

SECTION IV

CHARACTERIZATION OF THE WASTEWATERS

The characterization of a wastewater stream from an industrial process includes determination of the physical, chemical, and biological properties of the effluent in sufficient detail to allow the engineering of treatment processes. A survey of the wastewater from several of the hydrolyzer trains, operating on ethylene and propylene feed stock, was made to determine the properties. This survey was conducted so that the effects of the operating conditions on the quality of the waste stream were reflected. A description of the analytical methods used in this study and of the quality control techniques applied, are given in Appendix A.

Sampling and Analyses

Composite samples were collected from several of the operating plants over 24-hour periods during the week and 72-hour periods during the weekend. The sampling period extended from July 1 to September 12, 1969.

The measured analyses of the wastewater from those plants producing ethylene glycol are given in Table IV-1, and from those plants producing propylene glycol in Table IV-2. The results are tabulated to show the number of samples from each plant and the range and average values for each parameter.

The variation of the organic matter concentration in the effluents is rather wide, while the pH, % NaCl, and total dissolved solids (TDS) vary very little since they are easier to control in the process. The pH of the wastewater is 11.2 to 11.5, while the excess alkalinity, as sodium hydroxide, varies from 0.05% to 0.45%.

The principal organic materials in the ethylene system wastewater are glycol (averaging over 1000 ppm.) and dichloroethyl ether (averaging 29 ppm.). Ethylene oxide, dichloride, and chlorohydrin are not detected in most of the samples, and, when found, are in very low concentration.

In all the samples collected in the propylene system, the wastewater was found to contain the glycol, the oxide, and the epichlorohydrin. The high concentrations of organics in the wastewater from Plant (X), which is an experimental train, are reflected by the changes being made in the plant operation to study methods for reducing total organic losses. The ranges of concentrations found in the wastewater from Plant (Y) reflect normal operating conditions at full production capacity.

Preceding page blank

TABLE IV-1

ETHYLENE SYSTEM WASTEWATER
(COMPOSITE ANALYSES)

		No. of Samples	Minimum	Maximum	Average
% NaCl	(B)	37	9.2	11.46	10.72
	(A)	14	12.3	13.40	12.90
TDS, %	(B)	28	9.36	11.87	11.12
	(A)	9	12.87	13.81	13.30
Sp.Gr./30°C	(B)	37	1.062	1.077	1.072
	(A)	9	1.084	1.089	1.087
COD, ppm.	(B)	37	1120	2240	1630
	(A)	13	1160	3200	1850
TOD, ppm.	(B)	24	1310	2480	1730
	(A)	13	1110	3000	1920
E.G., ppm.	(B)	37	680	1470	1003
	(A)	14	720	2300	1306
E.O., ppm.		12	30	100	60
			(nil in 39 samples)		
EDC, ppm.		7	5	50	16
			(nil in 44 samples)		
ECH, ppm.		23	5	30	15
			(nil in 28 samples)		
DCEE, ppm.		47	10	90	29

(B) - First ethylene system.

(A) - Second ethylene system.

E.G. - Ethylene Glycol
E.O. - Ethylene Oxide
EDC - Ethylene Dichloride
ECH - Ethylene Chlorohydrin
DCEE - Dichloroethyl Ether

TABLE IV-2

PROPYLENE SYSTEM WASTEWATER
(COMPOSITE ANALYSES)

		No. of Samples	Minimum	Maximum	Average
% NaCl	(X)	41	8.5	10.7	9.8
	(Y)	14	9.8	10.6	10.3
TDS, %	(X)	28	9.51	10.82	10.1
	(Y)	9	10.20	11.04	10.65
Sp.Gr./30°C	(X)	40	1.0647	1.0693	1.0660
	(Y)	9	1.0682	1.0725	1.0716
COD, ppm.	(X)	37	1136	6160	3086
	(Y)	14	1550	3280	2138
TOD, ppm.	(X)	27	1910	7150	4398
	(Y)	14	1590	3350	2198
PG, ppm.	(X)	37	355	2550	1140
	(Y)	14	750	1620	960
PO, ppm.	(X)	30	10	390	196
	(Y)	14	10	70	28
EPCH, ppm.	(X)	37	38	400	138
	(Y)	14	0	80	25
PCH, ppm.		16	13	70	42
			(nil in 35 samples)		
PDC) DCIPE)			(nil in all samples)		

(X) - First propylene system.

(Y) - Second propylene system.

PG - Propylene Glycol
PO - Propylene Oxide
EPCH - Epichlorohydrin

PCH - Propylene Chlorohydrin (two isomers)
PDC - Propylene Dichloride
DCIPE - Dichloroisopropyl Ether

The analyses of the organic components in the wastewaters did not always account for the high values of COD and TOD. The gas chromatographic results were checked against a periodate oxidation method able to detect the oxide, the glycol and the chlorohydrin.

For the ethylene system (Table IV-3), the periodate and gas chromatographic results checked very well for the analysis of the glycol. The periodate method yielded higher values for the oxide and the chlorohydrin. As an example, the theoretical oxygen demand of the organic compounds detected in the first sample was calculated as follows:

	Analysis, ppm.	
	Periodate	Gas Chromatographic
EG	1033 x 1.288 = 1330	1100 x 1.288 = 1420
DCEE	20 x 1.23 = 25	20 x 1.23 = 25
ECH	28.6 x 1.093 = 31	10 x 1.093 = 11
EO	5.2 x 1.819 = 9	5.2 x 1.819 = 9
Theoretical O_2 Demand, ppm.	1395	1465

Both the COD and TOD of this sample were 1600 ppm., thus the organics detected account for 91.5% of the COD of the sample.

In the case of the propylene system (Table IV-4), the periodate method always yielded higher values for the glycol concentration than those determined by gas chromatography. A sample from the propylene wastewater had a theoretical oxygen demand of 2744 ppm. based on the periodate analysis, which accounts for 93.2% of the TOD of 2950 ppm.

Some of the wastewater samples from the propylene system contained other organics that were not detected by the developed VPC method. These other materials were separated on a modified column after acidifying the sample and were identified as acetol and acetic acid. The amount of these components varied with the age of the sample and are believed to be oxidation products of the major organic components of the wastewater.

Biological Oxidation of Organics in the Wastewater

A standard 5-day biological oxygen demand (BOD_5) test was run on several of the composite samples collected during the period extending from July to September, 1969. The seed used in the BOD bottles was a raw sewage sludge acclimated for a period of at least three days to the diluted waste stream.

TABLE IV-3

ORGANICS IN ETHYLENE SYSTEM WASTEWATER

Sample No.	Plant No.	COD ppm.	TOD ppm.	EG, ppm.		EO, ppm.		ECH, ppm.	
				G.C.	Periodate	G.C.	Periodate	G.C.	Periodate
1	(B)	1600	1600	1100	1033	0	5.0	0	28.6
2	(A)	1760	1750	900	1023	0	10.0	20	80
3	(A)	1680	1620	990	1010	0	0.0	20	0
4	(A)	1680	1740	1090	1080	0	0.0	20	0
5	(A)	1520	1510	1080	1090	0	0.0	0	20
6	(A)	1880	1770	1190	1180	0	10.0	10	120

COD - Chemical Oxygen Demand
TOD - Total Oxygen Demand
EG - Ethylene Glycol
EO - Ethylene Oxide
ECH - Ethylene Chlorohydrin
G.C. - Gas Chromatograph

TABLE IV-4

ORGANICS IN PROPYLENE SYSTEM WASTEWATER

Sample No.	Plant No.	COD ppm.	TOD ppm.	PG, ppm.		PO, ppm.		PCH + EPCH, ppm.	
				G.C.	Periodate	G.C.	Periodate	G.C.	Periodate
1	(X)	2800	2950	1070	1402	90	76	70	157
2	(X)	2360	2320	1040	1290	10	30	0	0
3	(X)	2600	2660	1050	1460	0	0	0	0
4	(X)	1920	2130	990	1173	90	30	0	0
5	(X)	2640	2700	450	760	390	190	70	800
6	(Y)	2240	2260	820	1220	60	0	40	0
7	(Y)	2240	2205	1000	1235	10	0	10	0
8	(Y)	2000	2060	910	1160	0	0	0	0
9	(Y)	2160	2350	990	1350	0	10	0	0
10	(Y)	2000	2060	810	1180	0	0	80	0

COD - Chemical Oxygen Demand
TOD - Total Oxygen Demand
PG - Propylene Glycol
PO - Propylene Oxide
PCH - Propylene Chlorohydrin
EPCH - Epichlorohydrin
G.C. - Gas Chromatograph

The results obtained for the wastewater from the propylene system are given in Table IV-5. The BOD_5 varied from 22% to 43.6% of the COD of the samples analyzed. The BOD_5 represents a fraction (0.5 to 0.8) of the calculated theoretical oxygen demand of the propylene glycol present in the sample. If it is assumed that the other organic components of the wastewater samples are not biodegradable, then the BOD_5 of the propylene glycol is 0.5 to 0.8 of its COD value. Several more samples of the propylene glycol wastewater were analyzed for BOD_5 during the operation of an activated sludge pilot plant. The correlation of the chemical and biological oxygen demands is shown in Table IV-6 to be:

$$BOD_5 = 0.36\ (TOD) + 5$$

The BOD_5 tests on several ethylene wastewater samples gave no response indicating that either a biological retardant or a poison is present in the wastes from the ethylene system.

The biological oxidation curve over a 10-day period was then determined with solutions of the organic components known to be present in the ethylene and propylene glycol wastes. Solutions containing about 100 parts per million of each compound were prepared and diluted 15 times in the BOD bottles, and 1 milliliter of an acclimated (3 days) sewage sludge seed was added to each bottle.

The results obtained with both ethylene glycol and propylene glycol are plotted in Figure IV-1. The 10-day BOD value represents 63.4% removal of ethylene glycol and 64.4% removal of propylene glycol.

The oxidation rates of ethylene oxide and propylene oxide are plotted in Figure VI-2. The 10-day BOD value represents a 30.8% oxidation of the ethylene oxide and only 12.4% oxidation of the propylene oxide. These values may be low due to the loss of the oxide by evaporation during the start of the test since the oxides have a low boiling point and are very volatile.

Ethylene dichloride, ethylene chlorohydrin, and the dichloroethyl ether gave negative BOD values as compared to the blank while the propylene dichloride, the epichlorohydrin, and the propylene chlorohydrin (1-chloro-2-propanol) yielded small positive BOD values over a 10-day period representing an oxidation of 3.5% to 7.5% of the theoretical oxygen demand.

A seed that has been acclimated to the ethylene glycol waste over a period of two months was used in the BOD bottles to determine the biological oxidation of the organic components in an ethylene glycol waste. Starting with the same concentration of each of the components, the ethylene glycol

TABLE IV-5

BIOLOGICAL AND CHEMICAL OXYGEN DEMAND OF WASTEWATER FROM PROPYLENE SYSTEM

Sample No.	COD[1]	BOD_5[2]	$\frac{BOD_5}{COD}$	Propylene Glycol, ppm.	Theor. O_2 Demand of PG	$\frac{BOD_5}{\text{Theor. } O_2 \text{ Demand of PG}}$
1	1580	560	0.354	540	907	0.617
2	2320	680	0.293	803	1350	0.505
3	4000	1450	0.363	1650	2760	0.525
4 (3)	4480	990	0.220	2400	4020	0.246
5	5830	2550	0.436	1900	3190	0.800

---

[1] - Two-hour permanganate oxidation.

[2] - Raw sewage seed acclimated for 3 days before test.

(3) - This sample contained a very high concentration of PO and EPCH which may explain the low BOD value.

TABLE IV-6

CORRELATION OF CHEMICAL AND BIOLOGICAL OXYGEN DEMAND PROPYLENE GLYCOL WASTEWATER

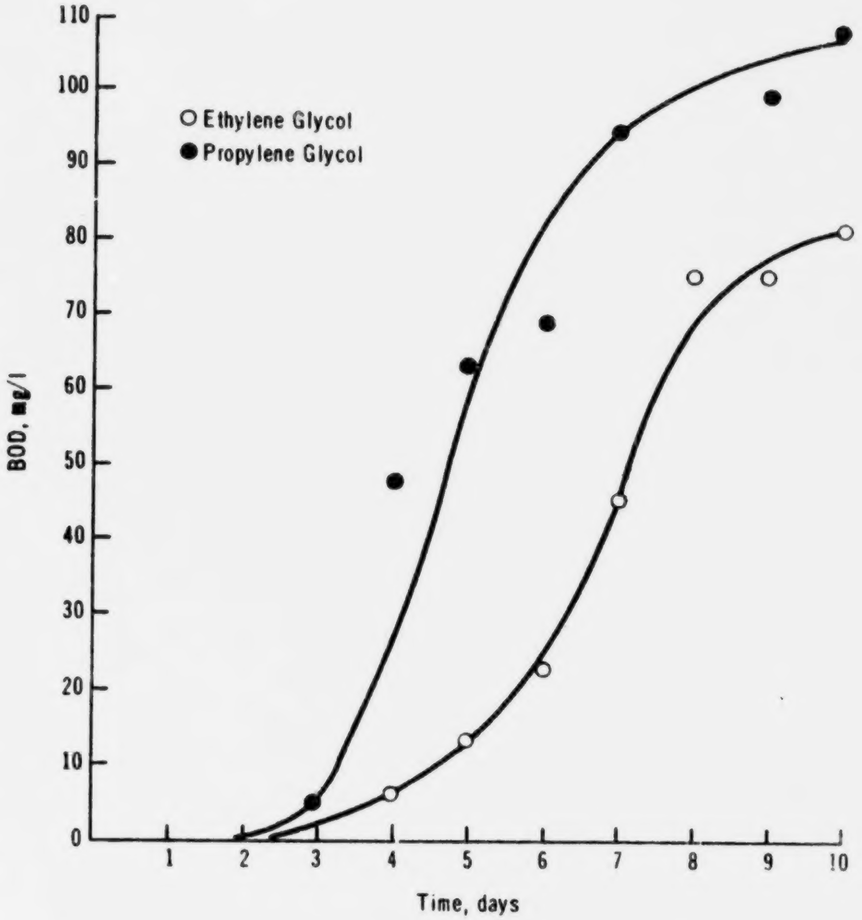
TOD or COD ppm	BOD_5 ppm
1580	560
2320	680
4000	1450
1256	658
1360	503
2020	1000
2300	814
1170	377
1470	475
1370	317

$$BOD_5 = 0.36\ (TOD) + 5$$

(correlation coefficient, r = 0.91;
<99.95% significant)

Figure IV-1

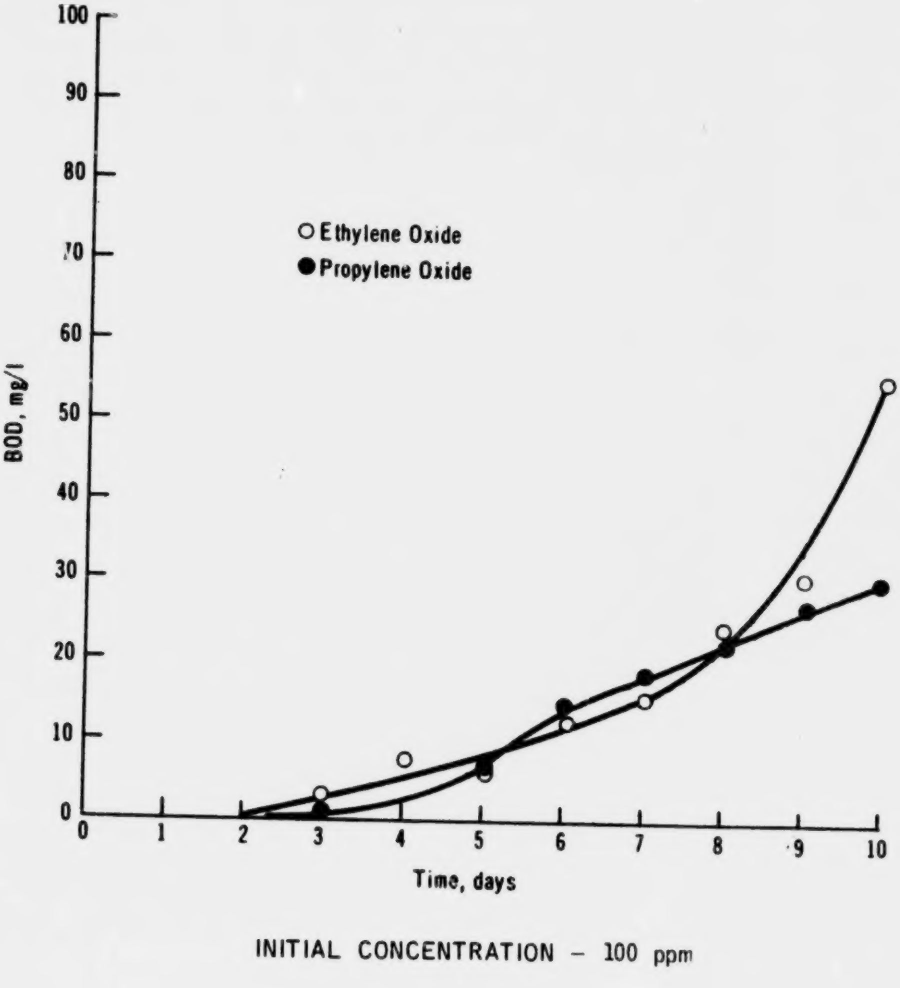
BIOLOGICAL OXIDATION OF ETHYLENE AND PROPYLENE GLYCOLS



INITIAL CONCENTRATION - 100 ppm

Figure IV-2

BIOLOGICAL OXIDATION OF ETHYLENE AND PROPYLENE OXIDES



INITIAL CONCENTRATION – 100 ppm

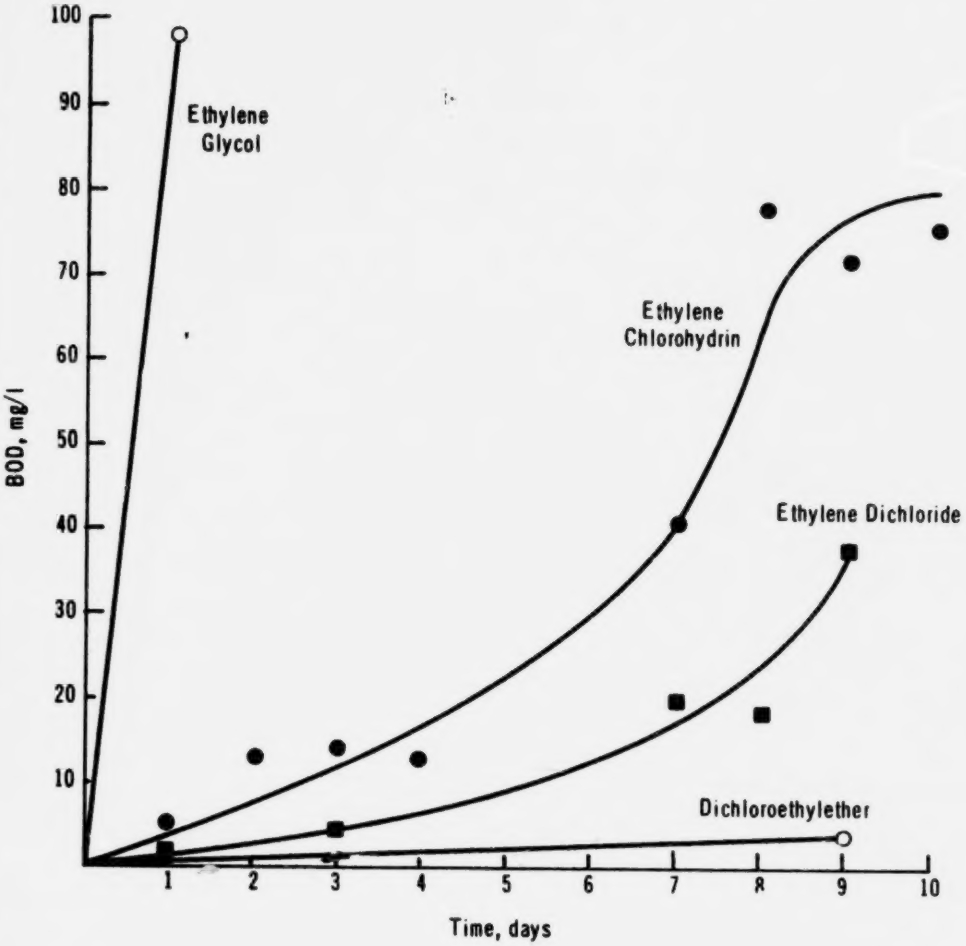
consumed practically all of the oxygen during the first day of the test. The results are plotted in Figure IV-3 over a period of 10 days. It is evident that ethylene chlorohydrin is biodegradable while the ethylene dichloride can be tolerated by the well acclimated culture and is partially oxidized. The dichloroethyl ether seems to be a poison.

Trace Elements in Waste Streams

Composite samples of the propylene and ethylene glycol wastewaters were analyzed for the trace elements that are important for the metabolism of bacteria and that may be toxic if present in high concentrations. An average analysis of these elements using emission spectroscopy is given in Table IV-7. It is concluded that the glycol waste streams do not contain any toxic quantities of trace metal ions and that the only required ingredients for bacterial growth in the waste media are the N and P nutrients.

Figure IV-3

BIOLOGICAL OXIDATION OF ORGANIC COMPONENTS OF THE ETHYLENE GLYCOL WASTE (Acclimated Seed)



INITIAL CONCENTRATION OF EACH COMPONENT – 100 ppm

TABLE IV-7

TRACE ELEMENTS IN TYPICAL GLYCOL WASTES

Element	Concentration ppm
Magnesium (Mg)	7.0
Calcium (Ca)	16.0
Iron (Fe)	1.0
Copper (Cu)	0.4
Zinc (Zn)	<2.0
Manganese (Mn)	<0.1
Molybdenum (Mo)	<0.1

SECTION V

RENOVATION AND PURIFICATION PROCESSES

The high salt content of the wastewaters from the production of polyhydric compounds makes it difficult to treat these waters by conventional methods. It has been believed that the wastewater must be diluted by a ratio of 1 to 6 to reduce the chloride concentration to below 10,000 ppm. in order for biological treatment to be possible. It has been previously recommended (Ford, 1971), that physical or chemical methods of treatment should be considered when the ratio of biological to chemical oxygen demand of the waste is in the range of 0.1 to 0.4. This ratio (BOD_5/COD) was found to be about 0.4 for the propylene glycol wastewater.

Several physical and chemical processes have been evaluated for the treatment of saline organic containing wastes. Chemical oxidation by the use of chlorine has been found to be technically unfeasible. Direct oxidation with ozone is able to affect a 90% reduction of COD in the waste, but at a prohibitively high cost. Extraction with conventional solvents has failed to allow separation of the glycol from the salt at the levels present in the waste streams and activated charcoal was found to have a very low capacity for glycol adsorption. Any wastewater renovation method that results in the separation of the sodium chloride from the main organic component, glycol, and at the same time yields a recoverable product is likely to be more attractive economically than those processes that eliminate or destroy the organic content.

Solvent extraction, adsorption and membrane separations were chosen as processes to be further studied for the treatment of the glycol wastewater and for possible further recovery of a usable product.

A. Solvent Extraction With Secondary and Tertiary Amines

The solvent extraction process as developed for the reclamation of saline water (Davison, 1960) and for the treatment of secondary sewage effluents (Zeitoun, 1964), operates on the principle that certain solvents which contain strong electronegative atoms within the molecule are partially miscible with water to an extent dependent on both the temperature and the salt content of the water. Secondary and tertiary amines of 5 and 6 total carbon atoms have been found to have, by far, the best solvent properties, (Davison, 1960).

Figure V-1 schematically shows the three major steps: extraction, separation, and solvent recovery. The solvent containing 8% water, as shown in Figure V-2, enters the bottom of the column and dissolves water as it rises countercurrently to the descending water phase. As the solvent leaves, it approaches equilibrium with the feed stream. The extract from the top of the column is heated to cause phase separation, and the solvent and water are decanted. The solvent is cooled and recycled, and the water goes to solvent recovery where the small amount of dissolved amine is recovered completely by steam stripping.

In Figure V-2, the solubility curve of diisopropylamine (DIPA) is shown. In this curve, the weight percent of water in the solvent is plotted against temperature for different salt concentrations. If one chooses an extraction temperature of 32°C, the solvent will dissolve approximately 30% water from the 1% salt solution. Heating the DIPA to 55°C will cause all but 8% of the water to phase out. After separation of the phases, recycling of the solvent makes the process continuous.

Solvent extraction, if applied to the wastewater from glycol production, could extractively separate both the glycol and water from the salt. The wastewater would then be concentrated to salt saturation and the glycol recovered in the low salt product water.

An engineering assessment could not be made because data were not available at these high salt concentration levels and the selectivity for glycol was not known. A laboratory investigation was undertaken to obtain the necessary equilibrium data to allow stage calculations.

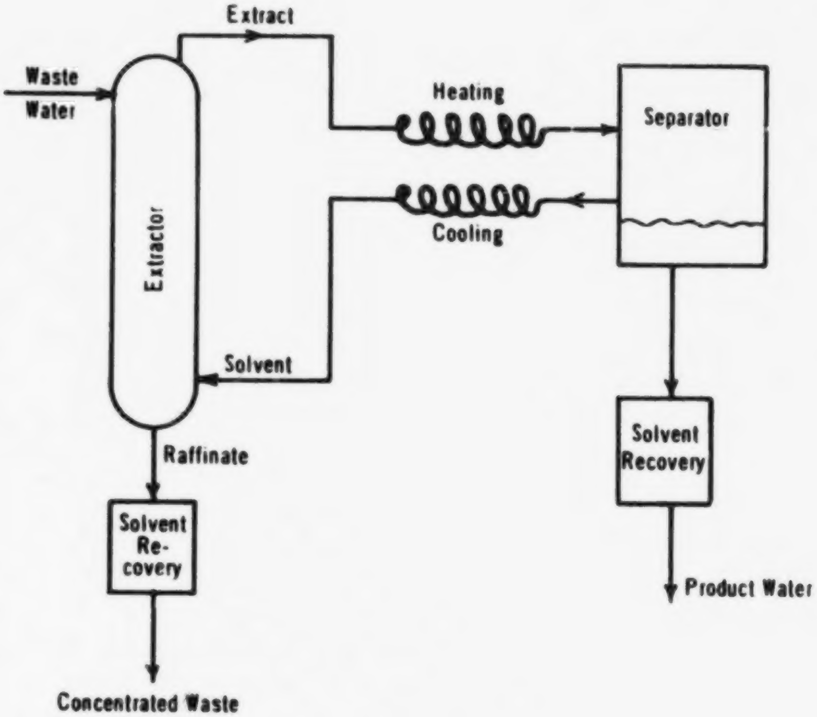
Diisopropyl Amine-Saturated NaCl Solution-Glycol System

Diisopropyl amine was equilibrated with a nearly saturated salt solution containing a known concentration of ethylene or propylene glycol. The solvent-salt mixture was well mixed in a water bath at a regulated temperature for at least four hours. The phases were separated, weighed, and analyzed for amine content, salt content, and glycol concentration. The salt and glycol concentrations in the feed, raffinate and product water are given in Table V-1 for propylene glycol and ethylene glycol at different temperatures.

The low temperatures used in these tests were necessary to enable the DIPA to pick up enough water at the high salt concentration. In every run except No. 6, salt precipitation was noticed, indicating that the aqueous phase became saturated.

Figure V-1

SCHEMATIC DIAGRAM OF THE SOLVENT EXTRACTION PROCESS


Extract
Waste Water
Heating
Separator
Extractor
Cooling
Solvent
Raffinate
Solvent Re-covery
Solvent Recovery
Product Water
Concentrated Waste

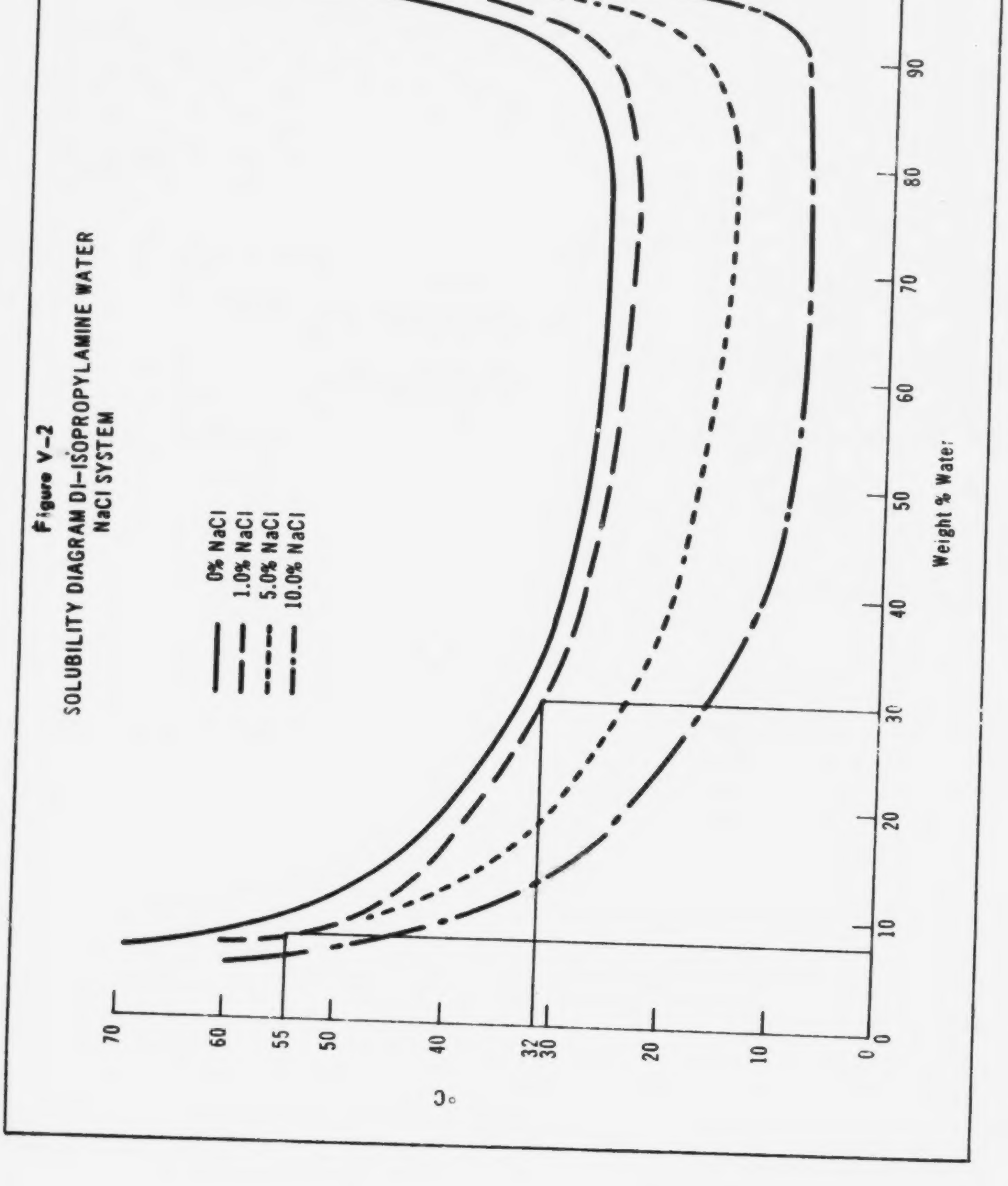


Figure V–2

SOLUBILITY DIAGRAM DI–ISOPROPYLAMINE WATER
NaCl SYSTEM

TABLE V-1

EQUILIBRIUM OF
DIISOPROPYL AMINE-SATURATED NaCl SOLUTION-GLYCOL

	Feed	Raffinate	Product[(a)]	K[(b)]
Run No. 1, (0°C)				
% NaCl	22.9	31.1	nil	--
Propylene Glycol, ppm	1640	147	8500	57
Run No. 2, (-5°C)				
% NaCl	23.1	26.0	9.64	0.37
Propylene Glycol, ppm	1770	550	5300	9.6
Run No. 3, (0°C)				
% NaCl	23.3	26.6	5.78	0.22
Propylene Glycol, ppm	1700	260	8600	33
Run No. 4, (-5°C)				
% NaCl	23.3	27.1	11.58	0.43
Propylene Glycol, ppm	1700	170	6000	35
Run No. 5, (-1°C)				
% NaCl	21.0	24.7	7.1	0.29
Ethylene Glycol, ppm	2400	500	8300	16.6
Run No. 6, (-5°C)				
% NaCl	22.9	27.4	10.7	0.39
Ethylene Glycol, ppm	2400	550	7100	12.9
Run No. 7, (10°C)				
% NaCl	22.9	24.9	7.2	0.29
Ethylene Glycol, ppm	2400	1010	21,300	21

Table V-1 (Continued)

	Feed	Raffinate	Product[(a)]	K[(b)]
Run No. 8, (0°C)				
% NaCl	22.9	27.1	8.2	0.30
Ethylene Glycol, ppm	2400	620	12,300	20

(a) Product obtained by distilling the amine from the extract.

(b) K; equilibrium constant for NaCl and the glycol is the ratio of concentration in the product to that in the raffinate calculated on solvent-free basis.

These results show that a high selectivity for the glycol in the solvent phase exists at the salt saturation stage of the extraction with no adverse effect on the salt selectivity. The raffinate, a saturated salt solution, would contain a very low concentration of glycol and thus may be directly usable as feed to chlorine cells. The product water separated from the extract by heating would have higher glycol concentrations and low salt concentrations and could be recycled to the glycol production plant, thus enabling recovery of the glycol from the waste stream.

Methyl Diethyl Amine-Saturated NaCl Solution - Ethylene Glycol System

Methyl Diethyl Amine (MDEA) is a tertiary amine with equivalent water - NaCl mixtures higher on the temperature scale than diisopropyl amine (DIPA). Therefore, MDEA can be used at higher temperatures to dissolve the same amount of water from a saturated NaCl solution than DIPA.

A sample of MDEA was obtained, purified and distilled, then used for the extraction of ethylene glycol from salt solutions. The MDEA was equilibrated with a nearly saturated salt solution containing a known concentration of ethylene glycol at 10° or 15°C. The raffinate was separated, then the extract was heated to 55-60°C to separate a product. The remaining solvent phase was then distilled to recover the rest of the glycol.

Table V-2 shows the results of three runs at 10° and 15°C. The material balance on the ethylene glycol shows about 25% of the glycol remaining in the raffinate. The glycol concentration in the product is two to three times the concentration in the raffinate, while the recycle solvent contained a high concentration of glycol calculated on solvent free basis.

This indicates that a lower equilibrium ratio for glycol in the product and raffinate exists than that obtained for diisopropyl amine, because the product in the previous experiments with DIPA was separated by distillation. The glycol will thus tend to accumulate in the solvent phase after a product separation which would require distillation of part of the flow of the solvent recycle.

Methyl Diethyl Amine - 10% NaCl Solution - Ethylene Glycol System

Another important equilibrium stage is that at the top of a column where the feed would be a 10% NaCl solution. The solvent phase would have a high concentration of glycol and a lower salt concentration.

TABLE V-2

EQUILIBRIUM OF
METHYL DIETHYL AMINE-SATURATED NaCl SOLUTION-ETHYLENE GLYCOL

	Feed	Raffinate	Product[(a)]	Solvent[(b)]
Run No. 1, 10°C				
Wt., grams	22.36	17.195	3.166	2.005
% NaCl	22.9	28.6	6.2	-
Ethylene Glycol, ppm	2150	650	1300	14,800
Run No. 2, 10°C				
Wt., grams	22.007	16.86	1.368	3.27
% NaCl	24.7	29.4	6.9	-
Ethylene Glycol, ppm	2190	1000	3100	8000
Run No. 3, 15°C				
Wt., grams	22.667	17.98	4.496	0.191
% NaCl	22.9	27.2	2.7	-
Ethylene Glycol, ppm	2150	590	1300	169,000

(a) Product separated from extract by heating to 55-60°C.

(b) Water separated from solvent by distillation.

Note: All concentrations are calculated on solvent-free basis.

A large volume of 10% NaCl solution containing a high concentration of ethylene glycol (≈4400 ppm.) was equilibrated with a samll volume of methyl diethyl amine (MDEA) at temperatures of 22° to 25°C. The results are given in Table V-3. The glycol concentration in the product remains higher than that in the raffinate, with some accumulation in the solvent phase. This indicates that in an extraction column the equilibrium with the feed at the top of the column results in a product with very low salt concentration and a relatively higher glycol concentration, and that the glycol will not tend to recycle in the extraction process since it keeps favoring the solvent phase at the top stage.

Solvent Extraction Design

Stagewise calculations were made for the extraction of ethylene glycol from the waste stream using methyl diethyl amine as the solvent. The extraction calculations were initially made considering salt as the solute to obtain flow rates and number of stages. Then, using equilibrium values for ethylene glycol, tray-by-tray calculations were made.

Assuming operating conditions corresponding to the obtained experimental data, (i.e., 25°C at the feed end and 10°C at the raffinate end and concentrating the brine to saturation), five theoretical stages were calculated to be required. A solvent-to-feed ratio of 5.74 was required and a saturated raffinate and a product water containing 2.5% NaCl and 2489 ppm. glycol were produced.

The resulting brine contained 860 ppm. glycol, using recycled solvent resulting from the phase separation at 60°C. Under these conditions the solvent contains appreciable glycol. With a lower glycol content in the solvent, a lower raffinate glycol content would be obtained.

Figure V-3 shows the stage calculation for sodium chloride using a coordinate system in which the X axis is:

$$\frac{\text{Salt}}{\text{salt + water}}$$

and the Y axis is:

$$\frac{\text{solvent}}{\text{salt + water}}.$$

Because of the small amount of solvent in the water phase, the water phase lies almost on the X axis. The solvent curve was averaged from the data. K values versus the Y axis were obtained from the data. Similar data were plotted for ethylene glycol. It is realized that for ethylene glycol, this plot is not exact, since K is a function of temperature, but since the operating temperatures are assumed to correspond to the data, this should not matter.

TABLE V-3

EQUILIBRIUM OF METHYL DIETHYL AMINE-10% NaCl SOLUTION-ETHYLENE GLYCOL

	Feed	Raffinate	Product(a)	Solvent(b)
Run No. 1, 25°C				
Wt., grams	201.8	194.14	7.67	0.661
% NaCl	10.1	10.13	2.54	-
Ethylene Glycol, ppm	4450	4200	5400	36,400
Run No. 2, 25°C				
Wt., grams	203.2	194.66	8.55	0.759
% NaCl	10.0	10.22	2.4	-
Ethylene Glycol, ppm	4370	4000	7200	22,200
Run No. 3, 22°C				
Wt., grams	193.8	183.8	12.33	0.626
% NaCl	10.1	10.21	3.75	-
Ethylene Glycol, ppm	4450	3600	5200	26,600

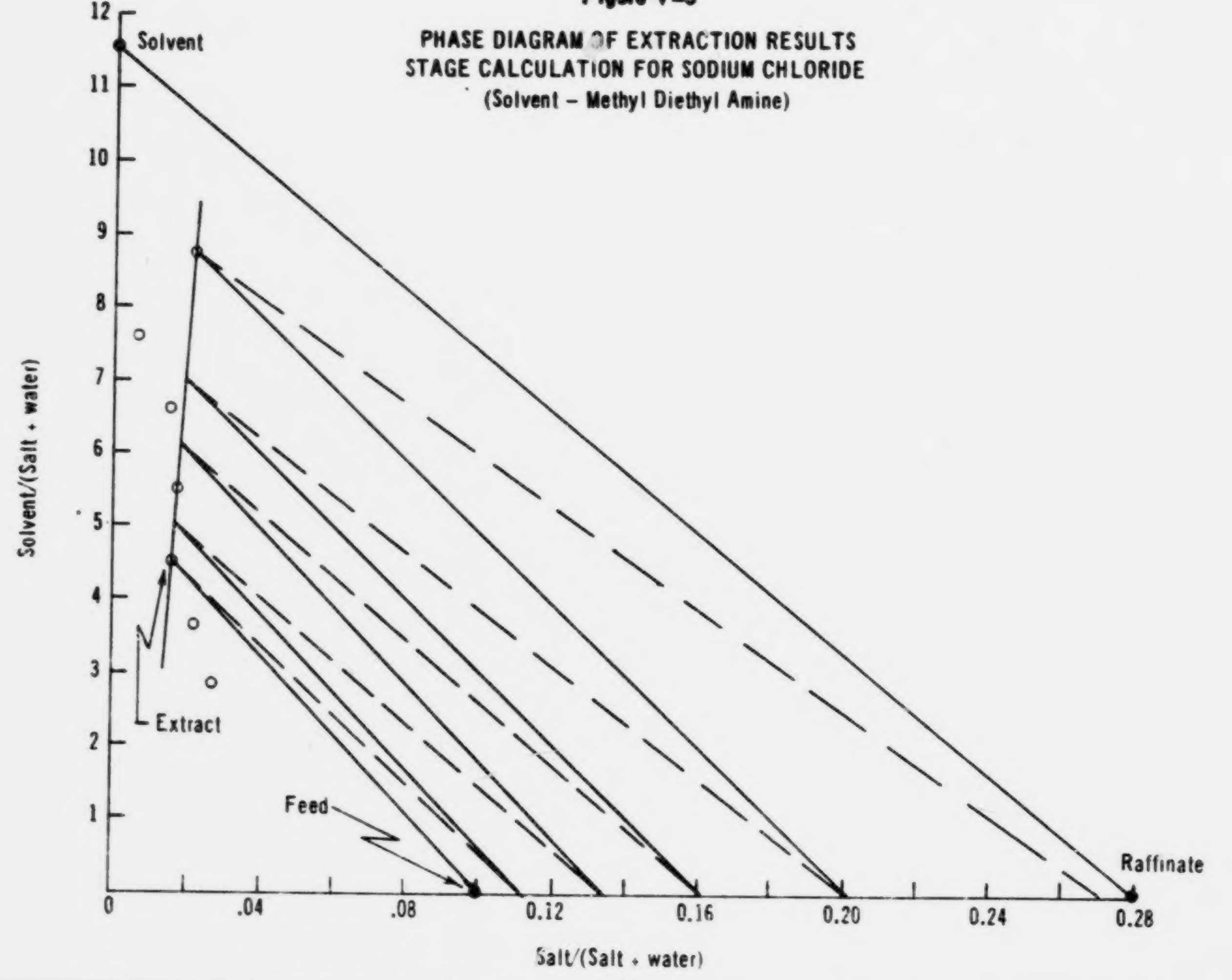
(a) Product separated from extract by heating to 55-60°C.

(b) Water separated from solvent by distillation.

Note: All concentrations are calculated on solvent-free basis.

Figure V–3

PHASE DIAGRAM OF EXTRACTION RESULTS
STAGE CALCULATION FOR SODIUM CHLORIDE
(Solvent – Methyl Diethyl Amine)



Five stages were obtained for sodium chloride. This gives an extract nearly in equilibrium with the feed. From the flow rates obtained in this way, a trial and error stagewise calculation was made on ethylene glycol until the system was in close material balance. The overall material balance is:

Stream	Flow (Solvent-Free)	Salt	Glycol, ppm.
Feed	1	10%	2000
Extract	1.16		2400
Product	.7	2.5%	2489
Solvent	.46		2265
Raffinate	.3	28%	859

On a total flow basis, based on an extract containing 18% water and a solvent 8% water:

$$\frac{\text{Product}}{\text{Feed}} = .7$$

$$\frac{\text{Solvent}}{\text{Product}} = 8.2$$

$$\frac{\text{Solvent}}{\text{Feed}} = 5.74$$

The solvent flow rate could be greatly reduced by operating at a higher extract water content (lower temperature). It is uncertain how this would affect equilibrium. The only comparison is the 10°C and 15°C data at 27 to 29% salt and the 25° and 22°C data at 10% salt. In each case, the K's are of the same order of magnitude. The effect of lowering temperature more than offsets the water effect, confirmed by low K's at separation, so much lower solvent rates could be obtained only by dropping the temperature. The effect on salt content in the product of lowering the temperature will be adverse, and it appears likely that some extract reflux will be necessary.

Solvent extraction seems to be technically feasible but would be uneconomic due principally to the high solvent-to-feed ratio required to produce a NaCl-saturated raffinate. Operation at low temperatures, close to 0°C, represents an appreciable increase in the difficulty and cost of the extraction process. The necessity of high reflux to produce a pure product and the cost of solvent recovery from both the raffinate and product, added to the required large solvent inventory, and the low temperature operation make solvent extraction uneconomical for the treatment of wastewater from glycol production.

B. Carbon Adsorption

Preliminary laboratory tests of glycol adsorption on activated carbons resulted in the selection of Witco carbon (20-40 mesh) as the best adsorbent available. Although the adsorptive capacity of carbon for ethylene or propylene glycol appeared to be too small for economical operation, further studies of the kinetics of glycol adsorption in batch and column operation were conducted with the hope that a simple regeneration procedure could be found that would result in the recovery of a product, thus improving the economics of the process.

Ethylene and propylene glycol solutions of two different concentration levels were prepared with and without 10% salt. A volume of 200 milliliters of each solution was dispensed into 250-ml. glass stoppered bottles. About 5 grams of carbon were weighed accurately and added to each bottle. The bottles were then tightly stoppered and placed in an oscillating shaker for three days. Samples of all solutions were collected at intervals of from 1 to 72 hours and analyzed for glycol by gas chromatography. Batch carbon adsorption tests were also conducted with both ethylene and propylene glycol solutions in 10% NaCl, at pH's ranging from 2 to 12.

In Figure V-4 is plotted the ratio of glycol concentration remaining in solution to the original concentration (C_t/C_o) as a function of time. The initial rate of adsorption of propylene glycol is higher than that for ethylene glycol, and equilibrium seems to be reached in a shorter time.

The equilibrium capacity of carbon for propylene glycol from a 10% NaCl solution is 263 mg/gram of carbon while that for ethylene glycol is 118 mg/gram of carbon. The presence of 10% NaCl in the glycol caused a slight increase in the adsorptive capacity.

In Figure V-5, the ratio of propylene glycol concentration remaining in solution to the original concentration, C_t/C_o, is plotted as a function of time at different pH's. The uptake of both glycols increases with increasing pH's. An increase in pH quite probably results in an increase of the negative charges at the surface of the carbon, thus enhancing the adsorption of the positively charged glycols which are known to be hydrogen bonded with the water molecules.

Figure V-4

ADSORPTION OF GLYCOLS ON WITCO CARBON 20 x 40 MESH

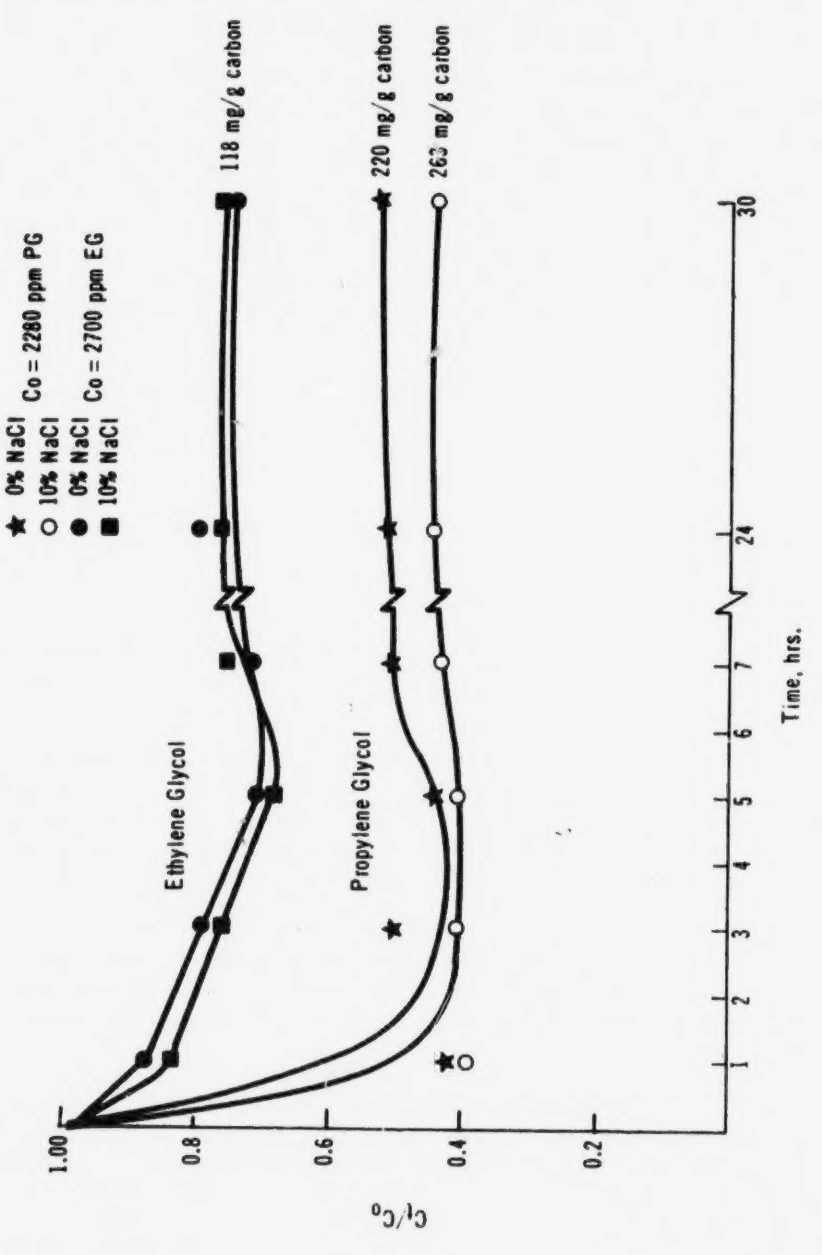
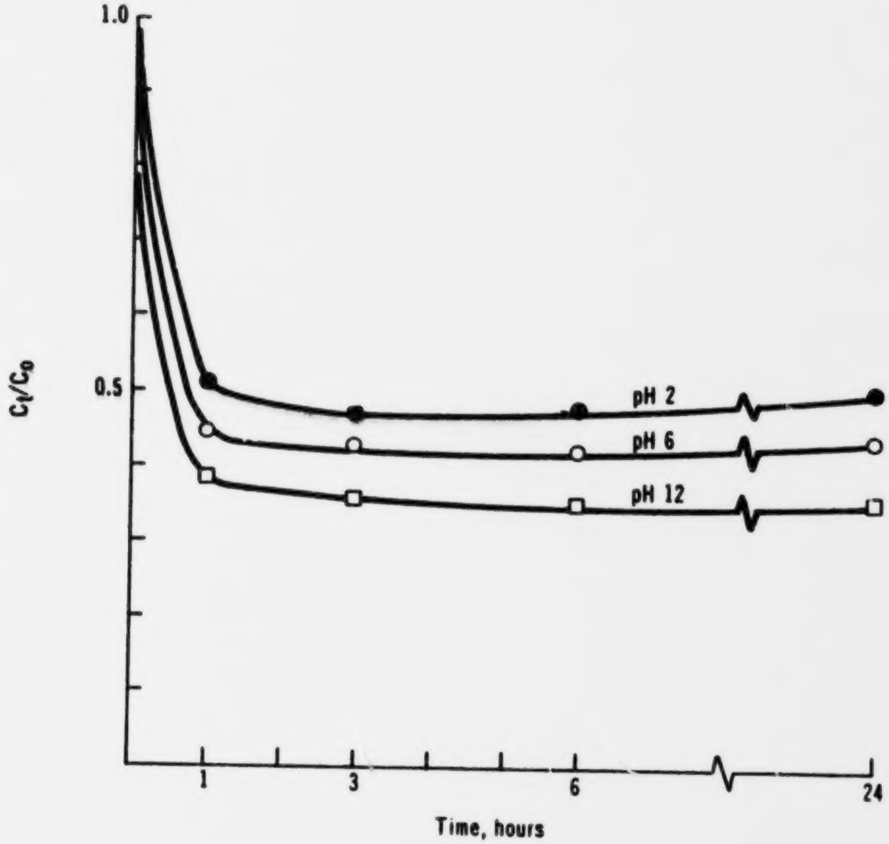


Figure V-5

EFFECT OF pH ON UPTAKE OF PROPYLENE GLYCOL BY WITCO CARBON 20-40 MESH. (C_o = 2000 ppm)



Fixed-Bed Column Adsorption of Glycols

The column adsorption of ethylene and propylene glycols from 10% NaCl solutions of pH 11.0 on 20 x 40 mesh Witco carbon was also studied. Methanol was used to regenerate the exhausted carbon and the glycol was recovered by distilling the methanol.

Propylene Glycol

A 7/8 inch i.d. column was packed with 18 inches (73 grams) of carbon. The propylene glycol solution was then passed through the column under constant pressure at a flow rate of 1.26 gal./min./ft.^{2}.

Samples of the effluent were collected periodically and analyzed. After saturation of the carbon with glycol, as determined by the breakthrough curves, the carbon was regenerated with two bed volumes of methanol at a flow rate of 0.57 gal./min./ft.^{2}. The carbon was then washed with several bed volumes of distilled water and another adsorption run repeated.

The results of eight adsorption regeneration cycles are given in Table V-4. Figure V-6 is a plot of the breakthrough of propylene glycol for the first and second adsorptions.

The capacity of carbon for propylene glycol was 66 milligrams of propylene glycol per gram of carbon for the first cycle, reduced by about 13% for the second run, then remaining constant at about 53 milligrams of propylene glycol per gram of carbon for the 8 runs reported in Table V-4. The exhaustion point remained the same--around 18 bed volumes--while a change in the position of the break point was observed. This may be due to incomplete regeneration. At room temperature, at least two bed volumes of methanol were required to recover the adsorbed glycol. At temperatures of 40° to 50°C, only one bed volume of methanol was sufficient to recover over 90% of the glycol.

Ethylene Glycol

The adsorption breakthrough curve for ethylene glycol from a column similar to that described for propylene glycol is given in Figure V-7 (I).

Because of the slow adsorption of ethylene glycol, another column was built with a carbon depth of 74 inches and an inside diameter of 1/2 inch. The ethylene glycol solution was passed through the column at a rate of 0.97 gal./min./ft.^{2}.

TABLE V-4

FIXED BED ADSORPTION OF PROPYLENE GLYCOL ON WITCO CARBON

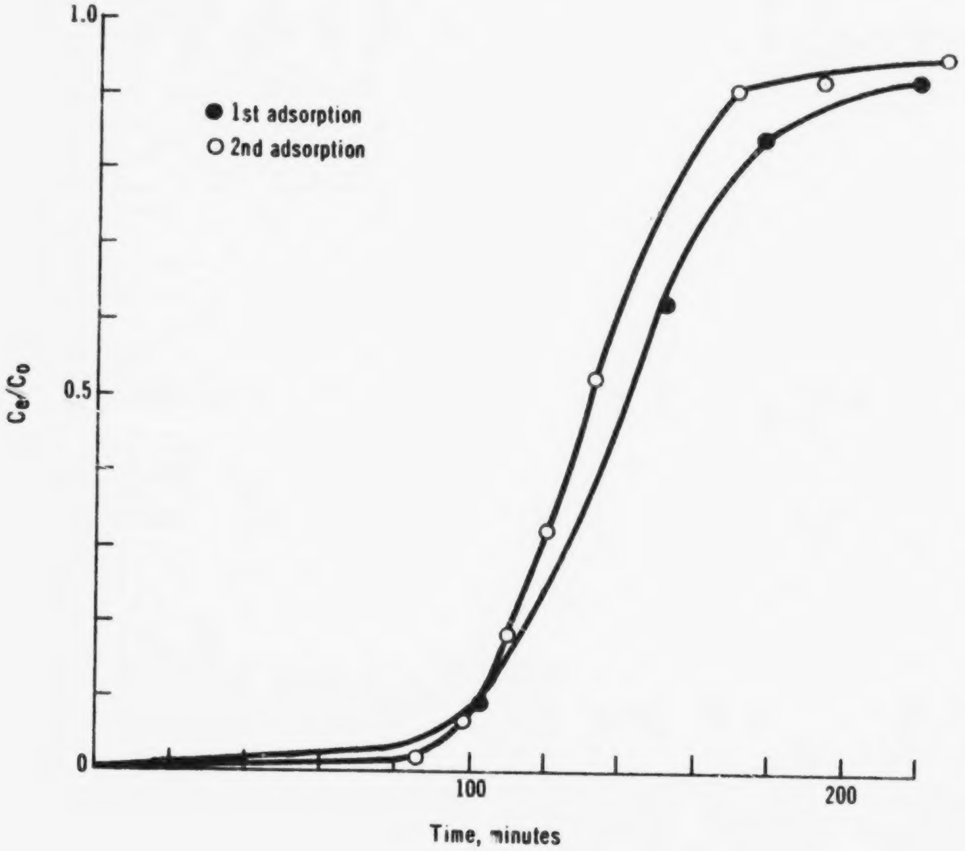
Run No.	Feed		Break Point		Exhaustion Point		Capacity (Mg PG/Gm Carbon)
	Flow Rate (GPM/Ft^2)	PG (ppm)	Time (Min.)	Bed Volumes	Time (Min.)	Bed Volumes	
1	1.29	1450	103	11.9	190	21.8	66
2	1.24	1340	100	11.0	180	19.9	53
3	1.17	1520	95	9.90	180	18.8	47.6
4	1.20	1600	95	10.2	185	19.8	52.9
5	1.14	1730	90	9.2	180	18.3	56.0
6	1.17	1580	80	8.4	150	15.6	53.3
7	1.20	1580	70	7.5	160	17.1	45.1
8	1.14	1600	80	8.13	180	18.3	51.3

Column = 7/8" i.d., 18" deep.

Wt. carbon = 73 grams.

Figure V-6

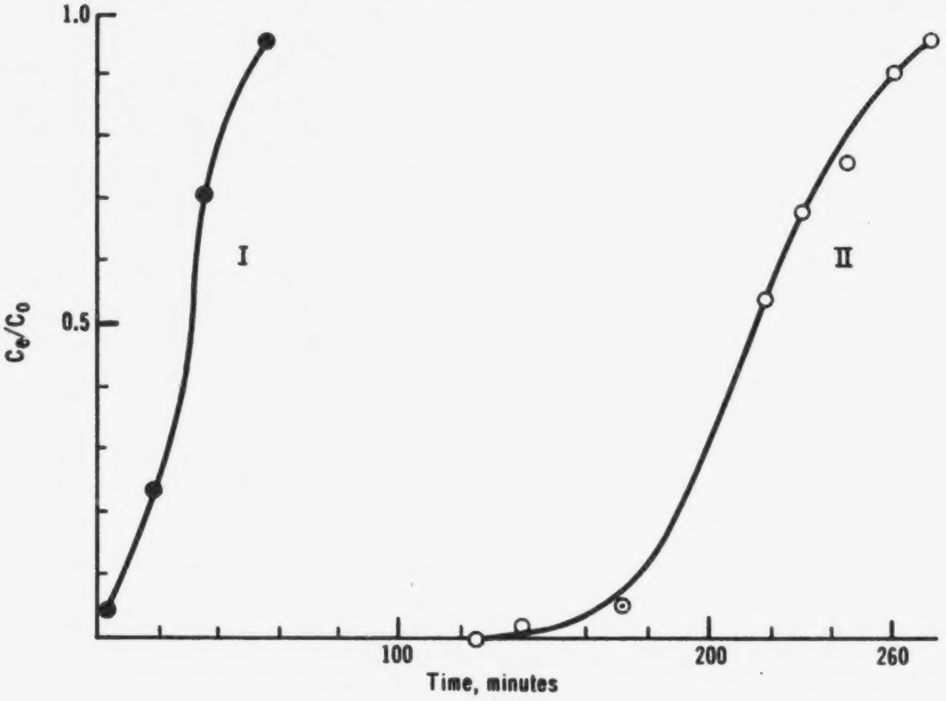
FIXED BED ADSORPTION OF PROPYLENE GLYCOL ON WITCO CARBON



Column: 7/8" i.d. depth = 18" Wt. carbon = 73 grams
Flow Rate: 1.26 gal/ft²/min.

Figure V-7

FIXED BED ADSORPTION OF ETHYLENE GLYCOL
ON ACTIVATED CARBON



I – Column: 7/8" i.d. 18" deep, Wt carbon = 73 grams, flow rate = 1.26 gal/ft²/min

II – Column: 1/2" i.d. 74" deep, Wt carbon = 97 grams, flow rate = 0.97 gal/ft²/min

The breakthrough curve obtained with this column is shown in Figure V-7 (II).

The total capacity of the carbon for ethylene glycol was calculated to be 14.9 mg/gram carbon, much smaller than the capacity obtained for propylene glycol. The capacity of activated carbon for ethylene glycol remained about the same through seven cycles--an average of 15 milligrams of ethylene glycol per gram of carbon, (Table V-5). The regeneration of the carbon with methanol required about one bed volume at ambient temperature, and over 90% of the adsorbed glycol was recovered.

Competitive Adsorption of the Chlorinated Hydrocarbons

A solution of 1200 parts per million ethylene glycol and 30 parts per million ethylene chlorohydrin (ECH) was passed through the 74-inch carbon column. The glycol breakthrough occurred after 3 bed volumes. No ECH was detected in the column effluent after 170 bed volumes. The ECH concentration was increased to 60 ppm., and after 260 bed volumes, it still had not broken through the column.

A solution of 1200 ppm. propylene glycol and 100 ppm. epichlorohydrin (EPCH) was passed through the 18-inch carbon column at a rate of 1.26 gallons per minute per square foot.

The propylene glycol broke through at about 7 bed volumes while EPCH was retained through 273 bed volumes. At this point the flow rate was increased to 4.1 gallons per minute per square foot, and the EPCH broke through after 23 bed volumes.

The capacity of activated carbon for ECH and EPCH is very high compared to the glycols. Similar tests with dichloroethylether and dichlorodiisopropylether showed a very high capacity of the carbon for the ethers over the glycols. The high adsorptive capacities found may be useful in removing the low concentrations of chlorinated hydrocarbons, that may be toxic, as a pretreatment before the activated sludge process.

Glycol Wastewater Treatment by Carbon Adsorption

Actual propylene glycol wastewater was fed to the 18-inch carbon column, packed with virgin Witco activated carbon. On the first pass 6.3 liters of propylene glycol waste was passes through the column before saturation with propylene glycol was obtained and 34.4 milligrams of propylene glycol was adsorbed per gram of carbon. The column was heated to 60°C and regenerated with hot methanol. Only 82% of the

TABLE V-5

FIXED BED ADSORPTION OF ETHYLENE GLYCOL ON ACTIVATED CARBON

Run No.	Feed		Break Time		Exhaustion Point		Capacity (Mg PG/Gm Carbon)
	Flow Rate (GPM/Ft^2)	EG (ppm)	Time (Min.)	Bed Volumes	Time (Min.)	Bed Volumes	
1	0.86	1450	130	2.45	--	--	14.9
2	1.11	1450	130	3.18	160	3.92	13.3
3	1.17	1600	120	3.10	160	4.14	15.1
4	1.15	1600	120	3.02	165	4.15	15.6
5	1.16	1480	120	3.07	166	4.24	14.5
6	1.16	1600	115	2.92	160	4.06	14.8
7	1.14	1670	117	2.91	160	3.98	15.4

Column = 1/2" i.d., 75" deep.

Wt. carbon = 97 grams.

propylene glycol was recovered. On the second run 6.5 liters of propylene glycol were passed before the column was saturated and 27.5 mg of propylene glycol was adsorbed per gram of carbon. On regeneration of the bed, 89% of the adsorbed propylene glycol was recovered.

From 5 to 7 bed volumes of water were required to remove the regeneration methanol from the bed. The capacity of carbon for propylene glycol from the wastewater feed is about half of its capacity when a synthetic propylene glycol solution is fed under the same operating conditions. This lower capacity is partly due to the lower propylene glycol concentration in the wastewater, and partly because of the competitive adsorption of the chlorinated organics in the waste stream.

Carbon adsorption is not considered to be economically feasible because of the low adsorptive capacity under the actual conditions and because of the inefficient regeneration and of the loss of solvent, if one is required.

C. Membrane Separations

During the period of the present grant, the State of Louisiana Department of Commerce and Industry, also had an R. and D. grant (Porject No. 12020 DQC) for the investigation of "Polymeric Materials for Treatment and Recovery of Petrochemical Wastes". Their results have been published by EPA, Report 12020 DQC-03/71. The objective of the reverse osmosis work conducted by their research contractor, Gulf South Research Institute, was to screen membranes that have a small reflection coefficient for NaCl, and to evaluate them for the rejection of the glycols and other organic components in the glycol waste stream.

Commerically available membranes having a small rejection coefficient for NaCl were evaluated with a synthetic solution containing:

NaCl, %	9.3 - 10.4
Propylene glycol, ppm.	500 - 2000
Propylene chlorohydrin, ppm.	20 - 70
Propylene oxide, ppm.	100 - 500

Samples from the tests conducted by GSRI were forwarded to us and analyzed for glycol content in our laboratories in Freeport, Texas. A summary of the results obtained from the screening tests on a flat plate cell are given in Table V-6. Most of these membranes were of Eastman cellulose acetate with low salt rejection.

TABLE V-6

EVALUATION OF CELLULOSE MEMBRANES FOR THE SEPARATION OF PROPYLENE GLYCOL AND SALT

Membrane Number	Operating Pressure p.s.i.	Flux GFD	Rejection, % NaCl	Rejection, % Organics
B112	600	7.5	9.5	5.5
B112	600	7.5	9.7	11.3
G16	800	54.5	5.5	0
G17	800	35.1	15.4	0
G19	800	29.5	20.7	20
G20	800	91.1	13.6	6.7
G21	800	21.1	21.0	0
G22	800	23.5	20	3.1
G23	800	10.5	35.6	13.2
G24	800	35.0	17.8	12.5
G25	800	12.4	55.7	41

Note: Data from Gulf South Research Institute EPA Report 12020DQC 03/71.

The results of this limited screening tests indicate the lack of rejection of the low molecular weight organic components. This may be due to the fact that when a membrane is selected to give a low enough NaCl rejection to reduce the osmotic effect to an acceptable level, pore flow becomes a dominant mode of transfer, therefore, very little separation of solutes is observed. It was concluded that membranes with low salt rejection exhibit a high pore flow of propylene glycol and thus offer no significant separation of the salt and the glycol.

SECTION VI

BIOLOGICAL TREATMENT

Since the glycol wastewater contains a large amount of salt, any organism that would be useful in biological treatment must be able to metabolize glycol in the presence of the high salinity. Dr. W. A. Taber of Texas A. and M. University isolated organisms from natural saline environments and from the waste carrying ditches and canals in the Dow plants, and screened them for their capacity to utilize glycols in the presence of high concentrations of salt. The results of this investigation are reported separately in Appendix E. The acclimation of mixed cultures to the glycol wastewater in both batch and continuous reactors was accomplished in the Dow laboratories at Freeport.

A. Biodegradability of Glycols in Saline Waters

The biodegradability of glycols, using an acclimated activated sludge seed, has been reported in the literature to vary from 35 to 85% (Mills, 1954 and Hatfield, 1957). A 96% oxidation of ethylene glycol and 39% oxidation of glycerol was obtained using a pure culture of Alcaligenes Faecalis (Marian, 1963). An activated sludge seed, under treatment plant conditions, was reported to oxidize 75% of the glycol present and 28% of the glycerol (Placak, 1947).

Activated sludges in a conventional biological system has been found to be much more tolerant to high salinities than an anaerobic digestion system. Operation of an activated sludge was found to be possible with salinities up to the equivalent of 2% NaCl (Ludzack, 1965). It has been found previously, however. that significant microbial population variety and activity changes occur at high salinities. The presence of sustained high chlorides generally depresses respiration, but periodic operation at low chlorides was found to improve the tolerance of activated sludge to high chlorides.

No information was found in the literature on the utilization of halophilic bacteria for the biological oxidation of organic contaminants in brine wastes, although numerous bacterial species living in very high salt concentrations have been investigated.

"Halobacterium", isolated from the Dead Sea, has an optimum NaCl concentration between 17.5 to 20.5% with a generation time of 4 hours. "H. salinarium", obtained from Norway, has an optimum NaCl concentration of 20 to 23%. A unicellular halophilic algae, "Dunaliella parva", was found to grow optimally in 6 to 9% NaCl with a generation time of one day. The requirement for NaCl does not appear to be entirely an osmotic phenomenon, since the bacteria were unable to tolerate the presence of sucrose instead of sodium chloride.

B. Treatability Studies

The biological treatability of wastewaters from ethylene and propylene glycol production plants was determined by the fill and draw procedure (Symons, 1960). A unit containing ten compartments, 2 inches wide by 5 inches deep by 18 inches high, was constructed of Plexiglas. The drawdown nozzles were at the 500 ml. level, and a mark was located at the 1500 ml. level. Each compartment was equipped with an aeration frit located near the bottom. The supply of oil free air, at reduced pressure, was manually adjusted to deliver about 0.55 liter of air per minute to each compartment.

Two cultures were acclimated to the glycol-sodium chloride solutions and the actual wastewater from the ethylene and propylene systems. In each set of test solutions, one compartment was not inoculated with bacteria and was used as a control.

Mixed Culture Acclimation

The starting culture was a mixture of sewage sludge and slimes obtained from the ditches and holding ponds exposed to the wastewaters from glycol production plants. The acclimation of this culture to glycol-sodium chloride solutions and diluted wastewater was begun at a salt concentration of about 3% which was raised gradually over a period of 6 weeks to the concentration of the full strength waste, about 10% salt. The feeding solution contained glycol as the main carbon source. Nutrients were added in the form of ammonium sulfate (0.25 gm/l.), and potassium hydrogen phosphate (0.25-0.375 gm/l.).

The wastewater-bacteria mixture was aerated for 23 hours, then the suspended solids were settled for 1 hour, and the supernatant drained to the 500 ml. level. Each compartment was then fed with 1,050 ml. of the prepared solution or diluted waste, with nutrients added and the pH controlled at 7.0. Aeration was then resumed and a sample collected within 5 minutes after pH adjustment. At the end of 23 hours of aeration, another sample was collected before the air was cut off. All samples were analyzed for pH, % NaCl, glycol and other organics, total oxygen demand, and volatile suspended solids.

During the acclimation period, the salt content was increased gradually up to the full strength waste, but the glycol concentration was kept the same as that in the waste. The daily composition of the treated waste and the rate of bacterial growth in each of the compartments dictated the rate at which changes in conditions were made.

The results obtained in the acclimations when full strength propylene glycol waste was fed are presented in Figures VI-1 and VI-2. A mixed liquor volatile suspended solids (MLVSS) of over 1000 ppm. could be maintained and settled quickly leaving a fairly clear supernatant. The loading-removal curve for propylene glycol waste (Figure VI-1) shows that biodegradation was accomplished with an efficiency of 91.2% by the well-acclimated mixed culture. A treated effluent of less than 200 ppm. TOD was produced at a loading of 1.0 to 2.0 pounds of TOD per pound of MLVSS per day (Figure VI-2).

Bacterium No. 52

This culture was isolated from mud-water samples from the Great Salt Lake, during the screening of microbes for tolerance to high salt content and glycol metabolism. Since this culture had already been acclimated to the full strength waste streams, no gradual acclimation to the salt was necessary. Bacterium No. 52 exhibited a dispersed phase growth with no appreciable settling when aeration was stopped, therefore, the fill and draw procedure used with the acclimated mixed culture had to be modified. Sufficient feeding solution was added to the testing compartments to replace the samples removed, but was enriched with glycol to replace the substrate oxidized. Near the end of these tests, it was found that reduction of the nutrient concentrations to less than half resulted in some improved settling of Bacterium No. 52. The supernatant was always very turbid.

The results obtained with ethylene and propylene glycol wastes are presented in Figures VI-3 and VI-4. A mixed liquor volatile suspended solids (MLVSS) of 1500 ppm. to 2500 ppm. could be maintained, but the filtered treated effluent had a high TOD concentration even when it contained no unreacted glycol.

Bacterium No. 52 showed a lower efficiency of TOD removal (88%) from propylene glycol waste and even lower (70%) from ethylene glycol waste (Figure VI-3) than the mixed culture. At a loading of 1.0 to 1.5 pounds TOD per pound MLVSS per day, the treated effluent contained over 300 ppm. TOD (Figure VI-4).

Figure VI-1

BIOTREATABILITY TESTS

LOADING - REMOVAL CURVE FOR PROPYLENE GLYCOL WASTE (NaCl 9-10.5%)

[Acclimated Mixed Culture]

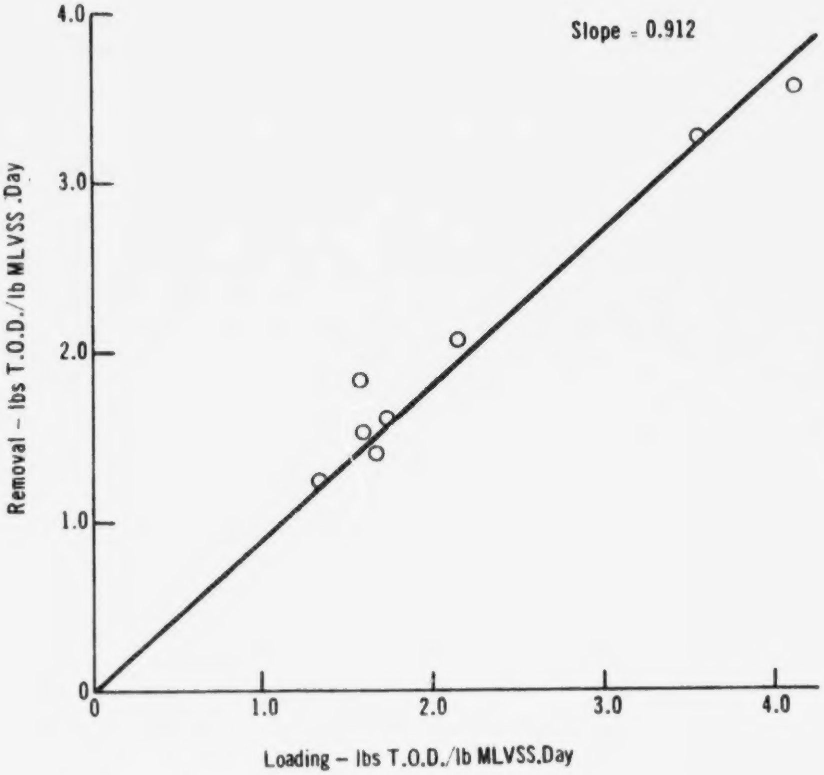


Figure VI-2

BIOTREATABILITY TESTS

EFFLUENT LOADING CURVE FOR PROPYLENE GLYCOL
WASTE (NaCl 9–10.5%)

[Acclimated Mixed Culture]

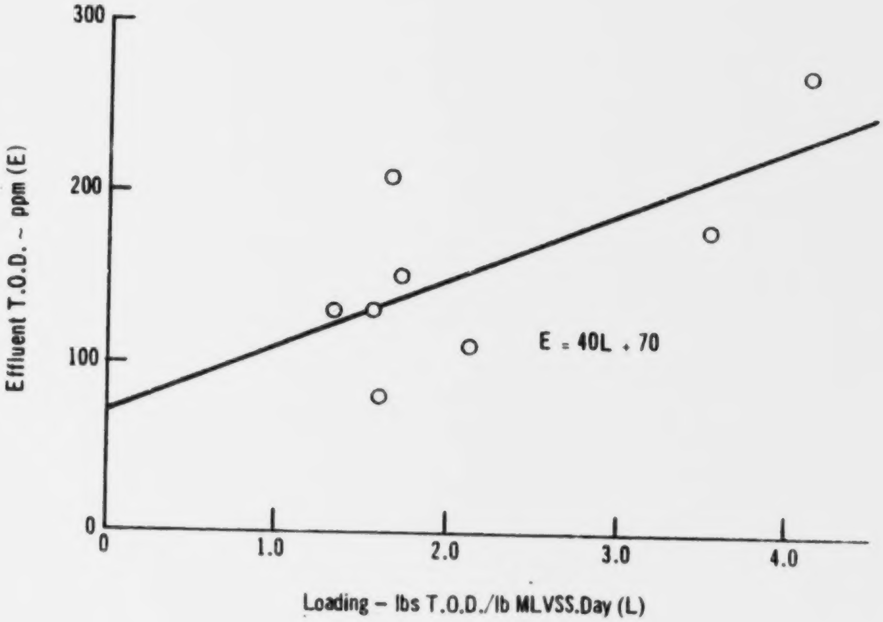


Figure VI-3

BIOTREATABILITY TESTS

LOADING – REMOVAL CURVES

○ Propylene Glycol Waste (NaCl 10–12%)

● Ethylene Glycol Waste (NaCl 11–13.5%)

[Bacterium No. 52]

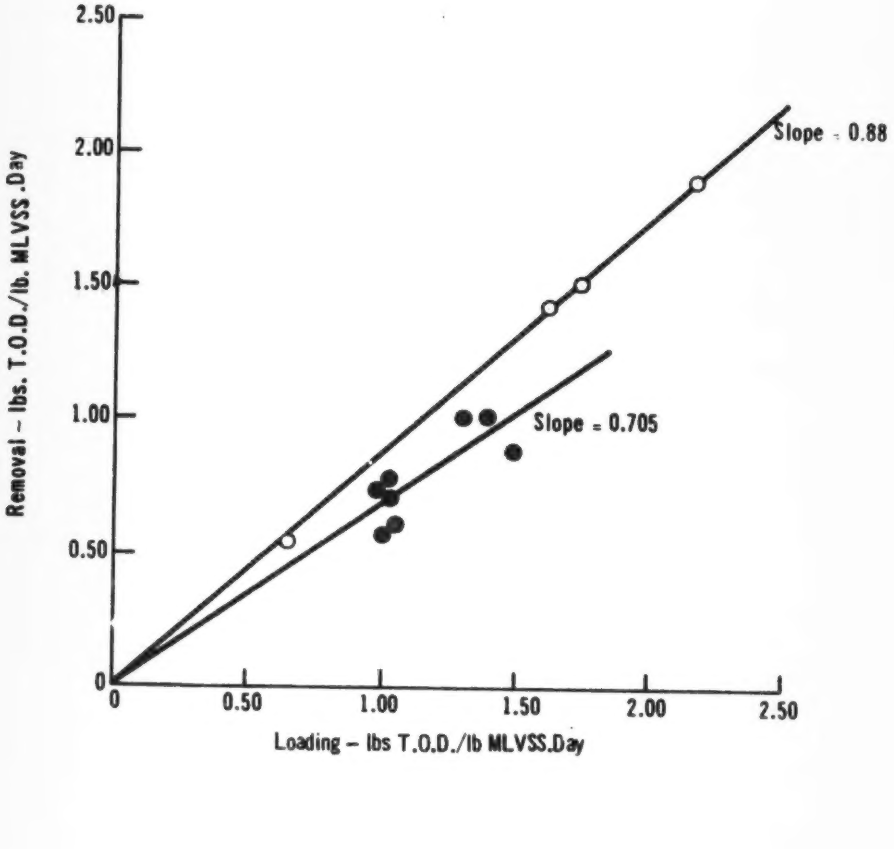


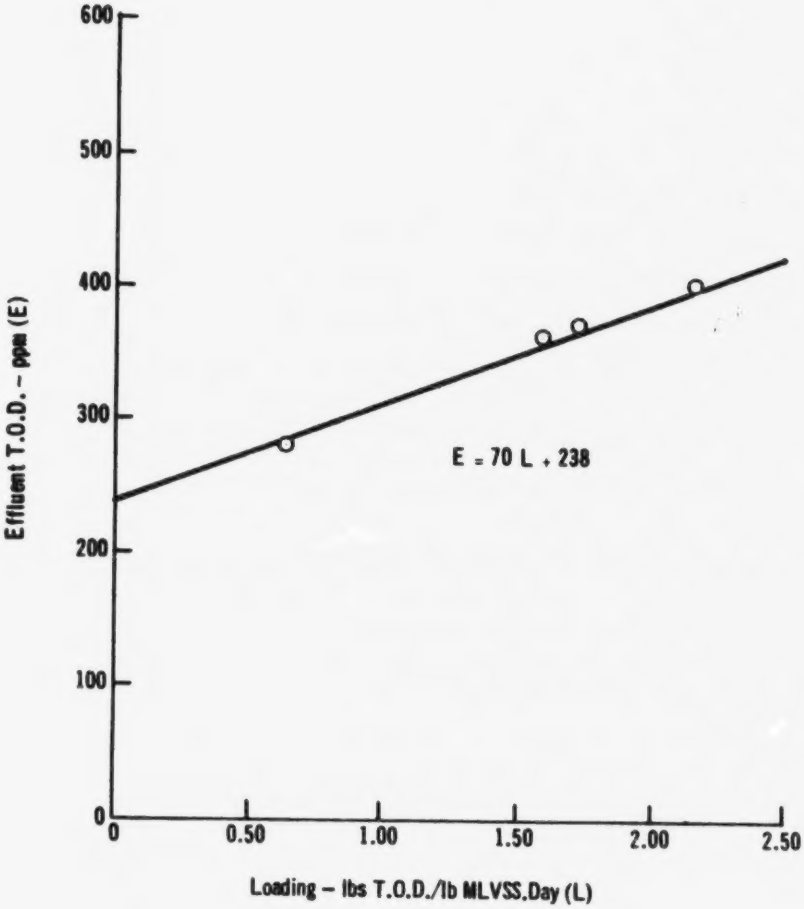
Figure VI-4

BIOTREATABILITY TESTS

EFFLUENT LOADING CURVE FOR PROPYLENE GLYCOL WASTE

(NaCl 10–12%)

[Bacterium No. 52]



C. Batch Kinetics

The rates of bio-oxidation of ethylene and propylene glycols in synthetic sodium chloride solutions and in actual glycol wastewaters was followed by measuring the decrease in glycol and TOD concentrations with time in the fill-and draw compartments used for the biotreatability tests.

The TOD removal from a propylene glycol-10% NaCl solution at a loading of 0.94 pounds TOD per pound MLVSS is shown in Figure VI-5. The method of calculating the rate of removal is illustrated in this figure, where r is defined by:

$$r = \frac{L_i - L_e}{L_e t_e}$$

where

r = rate of removal, 1/hr.

L_i = initial TOD concentration, ppm.

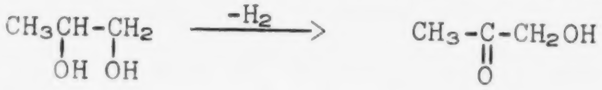
L_e = TOD concentration at equilibrium, ppm.

t_e = time to reach equilibrium, hr.

The equilibrium is established between the oxidation and synthesis reactions in which TOD is removed and the endogenous reactions where the end products of cell lysis return to the substrate. This model of TOD transfer rate in a batch biological oxidation system is adopted from Bhatla et. al. (1966).

In Figure VI-6 is shown a plot of the concentration of propylene glycol and an unknown metabolite as a function of time. The unknown metabolite that peaks around 5 to 6 hours after the propylene glycol feed is added, elutes from the VPC column at the same spot as epichlorohydrin.

The batch kinetics of a propylene glycol waste containing epichlorohydrin is given in Figure VI-7. The sum of the intermediate metabolite of the propylene glycol plus the epichlorohydrin is plotted in the lower curve. This metabolite has been identified by mass spectroscopy and gas chromatography as acetol. Traces of acetic acid were also detected in some of the intermediate samples. Acetol appears to be the first oxidation product of propylene glycol:



$$CH_3\underset{OH}{CH}-\underset{OH}{CH_2} \xrightarrow{-H_2} CH_3-\underset{\overset{\|}{O}}{C}-CH_2OH$$

Propylene glycol Acetol

Figure VI-5

BATCH KINETICS
PROPYLENE GLYCOL–10% NaCl
ACCLIMATED MIXED CULTURE

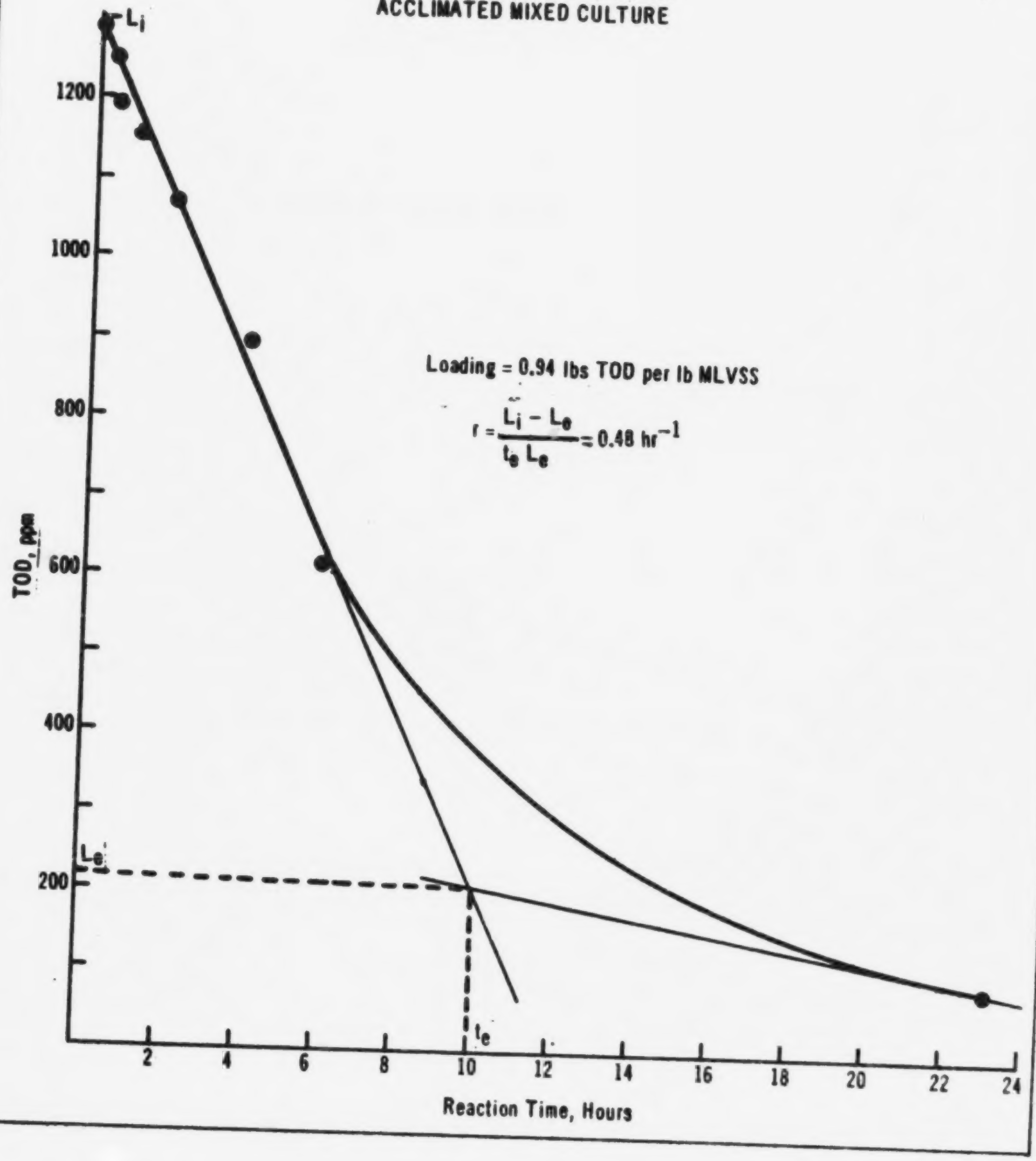


Figure VI-6

BATCH KINETICS
PROPYLENE GLYCOL-10% NaCl
ACCLIMATED MIXED CULTURE

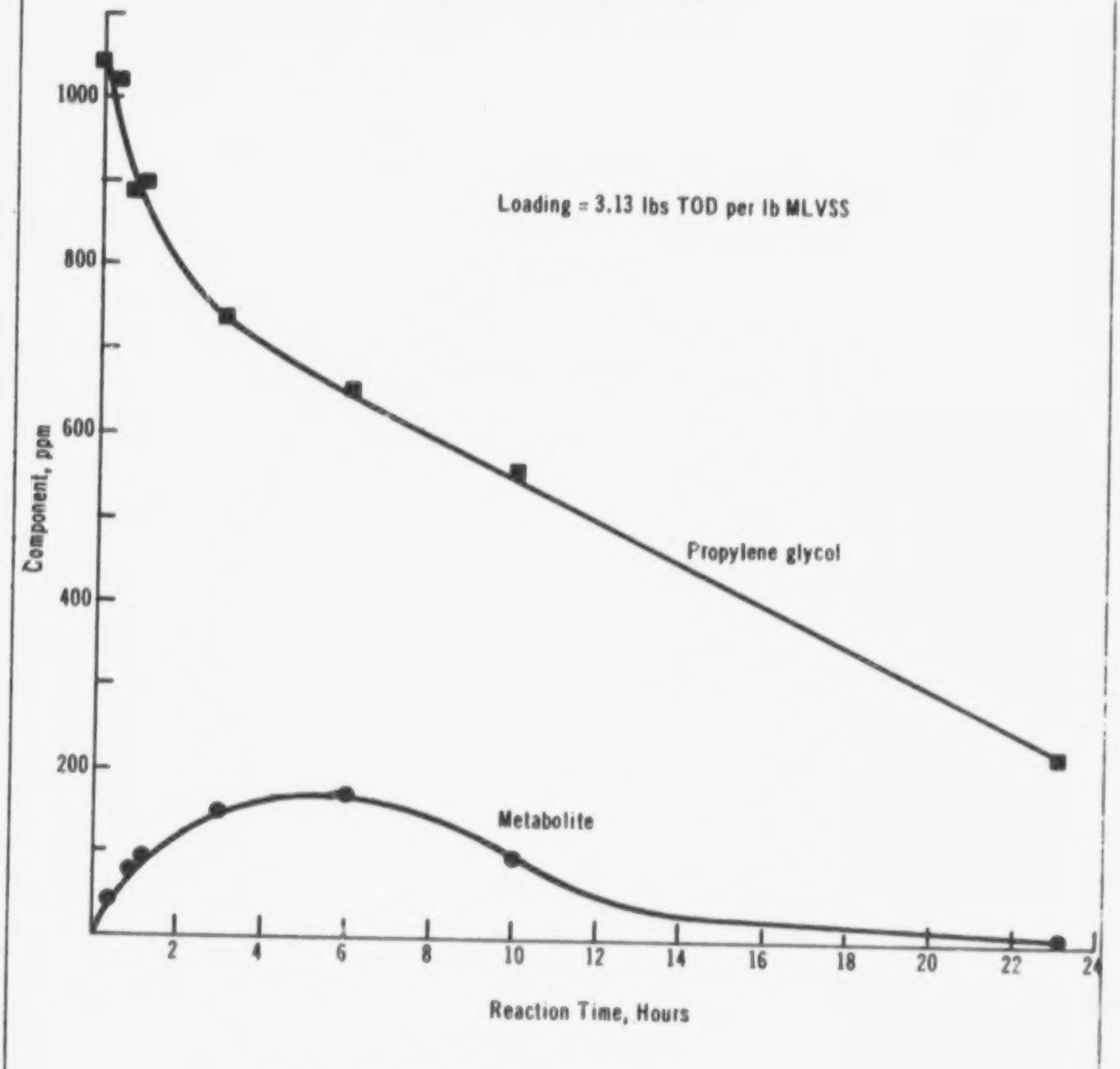
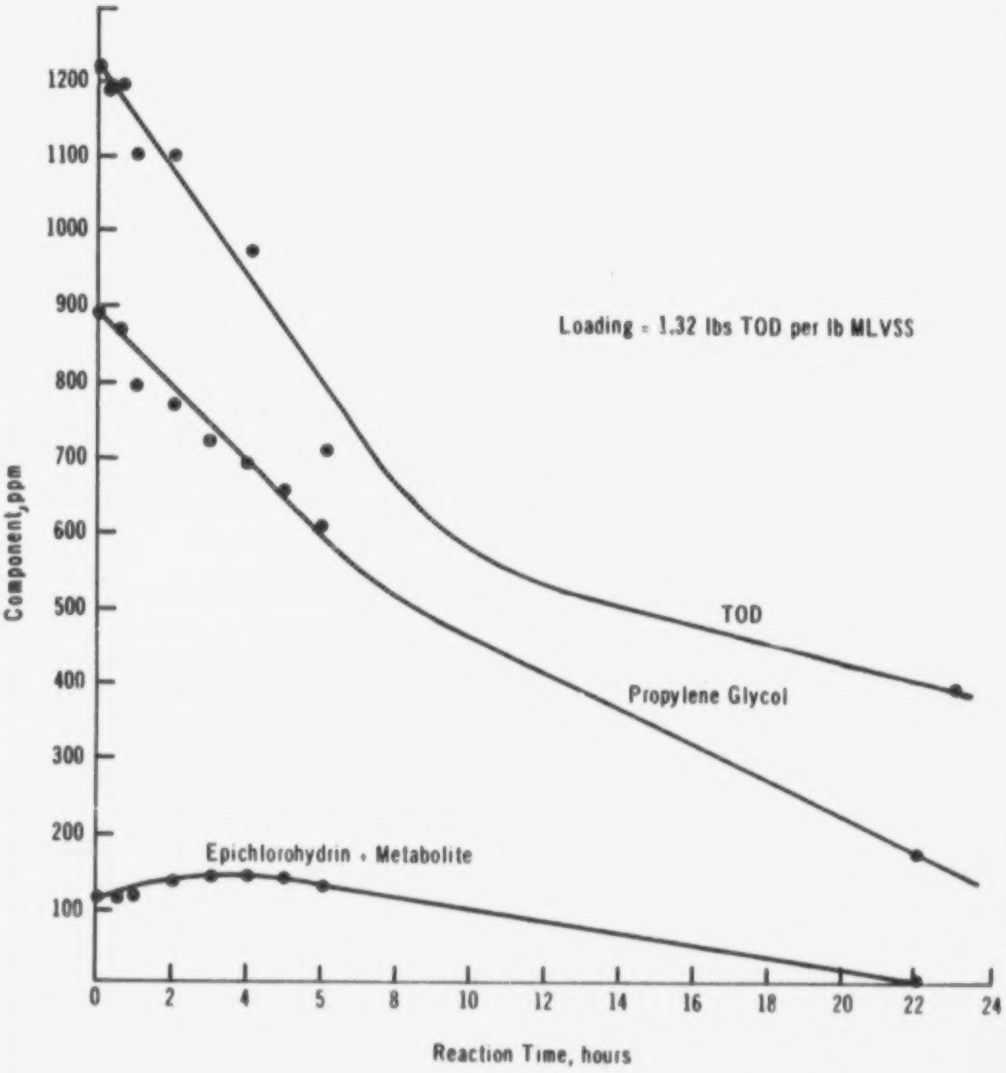


Figure VI-7
BATCH KINETICS
PROPYLENE GLYCOL WASTEWATER, ACCLIMATED MIXED CULTURE



Loading = 1.32 lbs TOD per lb MLVSS

The bio-oxidation rate of an ethylene glycol wastewater is shown in Figure VI-8, at a loading of 0.37 pounds TOD per pound MLVSS per day. The reaction rate of ethylene glycol is much slower than that found for propylene glycol.

The biological oxidation of a propylene glycol-10% NaCl solution with Bacterium No. 52 is presented in Figure VI-9. These results show a fast rate of propylene glycol removal, but the remaining TOD is high, a characteristic of the well dispersed Bacterium No. 52.

Effect of Dilution on Reaction Rates

Several runs were made using the acclimated mixed culture and Bacterium No. 52, at various dilutions of propylene glycol waste with river water, to observe the effect of lower sodium chloride concentrations on TOD removal rates. These dilutions were:

60% Wastewater - 40% River Water (6-6.5% NaCl)

75% Wastewater - 25% River Water (7-7.5% NaCl)

80% Wastewater - 20% River Water (8-8.5% NaCl)

The rates of TOD removal at various loadings and dilutions are given in Table VI-1 for both the acclimated mixed culture and Bacterium No. 52. Dilution of the propylene glycol wastewater to a salt content of 6 to 8% appears to increase the rate of TOD removal appreciably, for either of the two bacterial cultures used.

Calculation of Removal Efficiency in a Continuous Treatment From Batch Kinetic Data

The model used to calculate a rate constant at the equilibrium point is based on the assumption that the substrate equilibrium curve follows a first order relationship:

$$r = \frac{L_i - L_e}{t_e L_e}$$

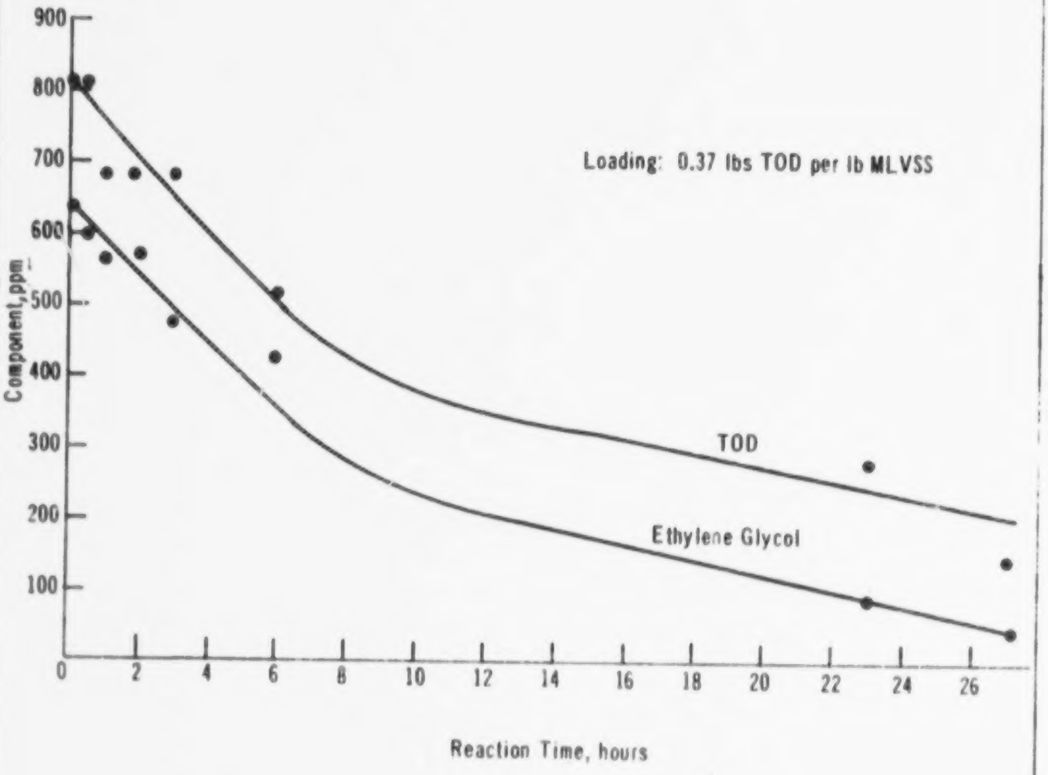
The rate constant, $r = 0.48\ \text{hr.}^{-1}$, for the propylene glycol system was used to calculate the degree of completion of the reaction, $D = 1 - (1-r)^t$, as shown in Figure VI-10.

To translate the batch reaction data to a continuous system, mixing kinetics in a continuous system must be utilized. A curve for complete mixing kinetics in a single basin is shown in Figure VI-11.

Figure VI-8

BATCH KINETICS

ETHYLENE GLYCOL WASTEWATER, ACCLIMATED MIXED CULTURE



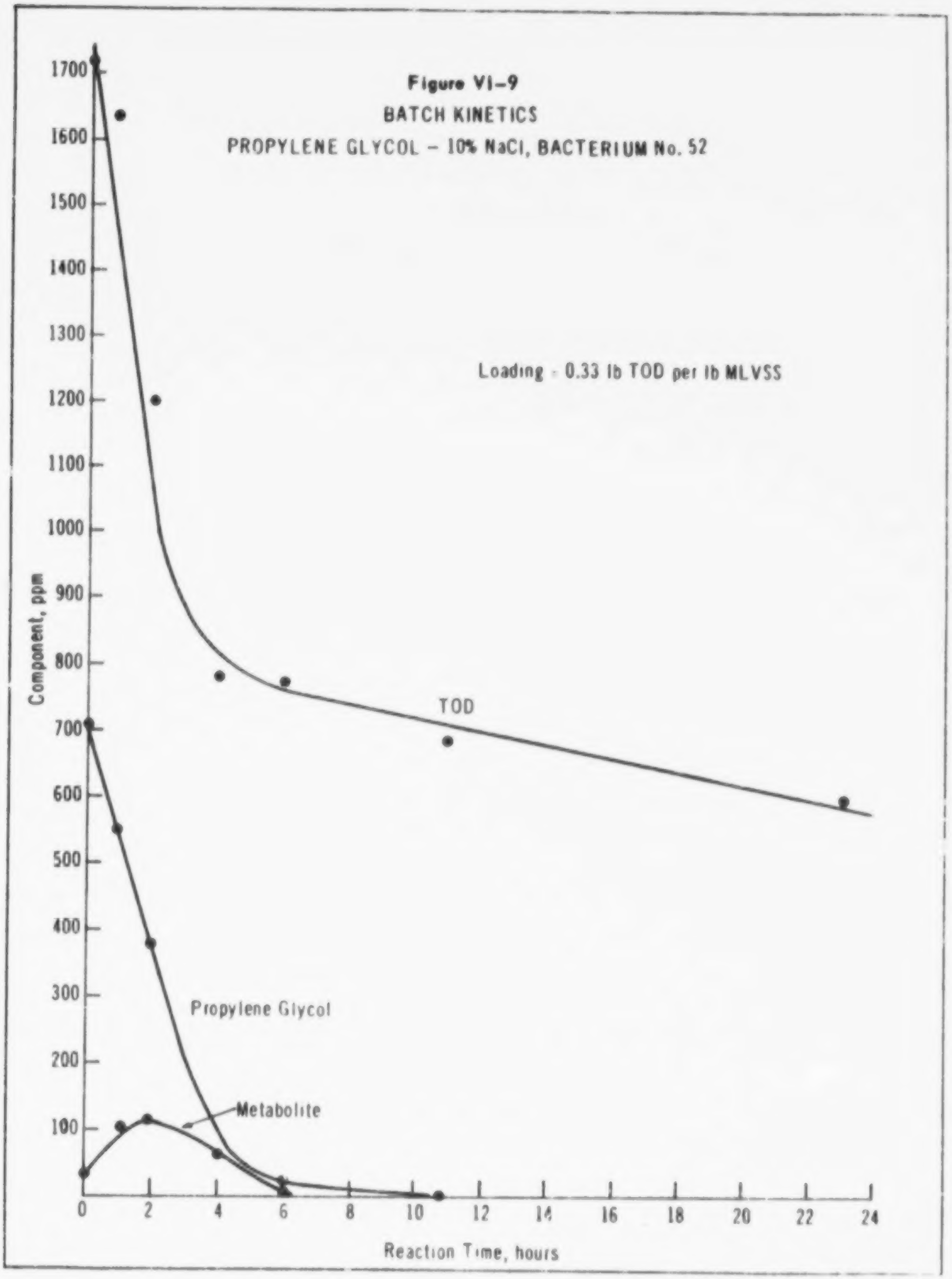


Figure VI-9
BATCH KINETICS
PROPYLENE GLYCOL – 10% NaCl, BACTERIUM No. 52

TABLE VI-1

BATCH KINETICS OF BIO-OXIDATION OF ETHYLENE AND PROPYLENE WASTEWATERS

Wastewater	% NaCl	Sludge	Loading Lbs. TOD/ Lb. MLVSS	Rate of TOD Removal r, hr.$^{-1}$
Ethylene Glycol	10	Mixed Culture	1.21	0.058
Ethylene Glycol	10	Mixed Culture	0.37	0.138
Propylene Glycol	10	Mixed Culture	1.32	0.130
Propylene Glycol	10	Mixed Culture	0.94	0.48
Propylene Glycol	10	Bacterium 52	0.33	0.44
Propylene Glycol	8.3	Mixed Culture	0.30	1.06
Propylene Glycol	6.1	Mixed Culture	0.43	0.80
Propylene Glycol	8.1	Bacterium 52	0.34	0.72
Propylene Glycol	7.5	Bacterium 52	0.34	0.76

Figure VI-10

BIOLOGICAL REACTION RATE OF
PROPYLENE GLYCOL

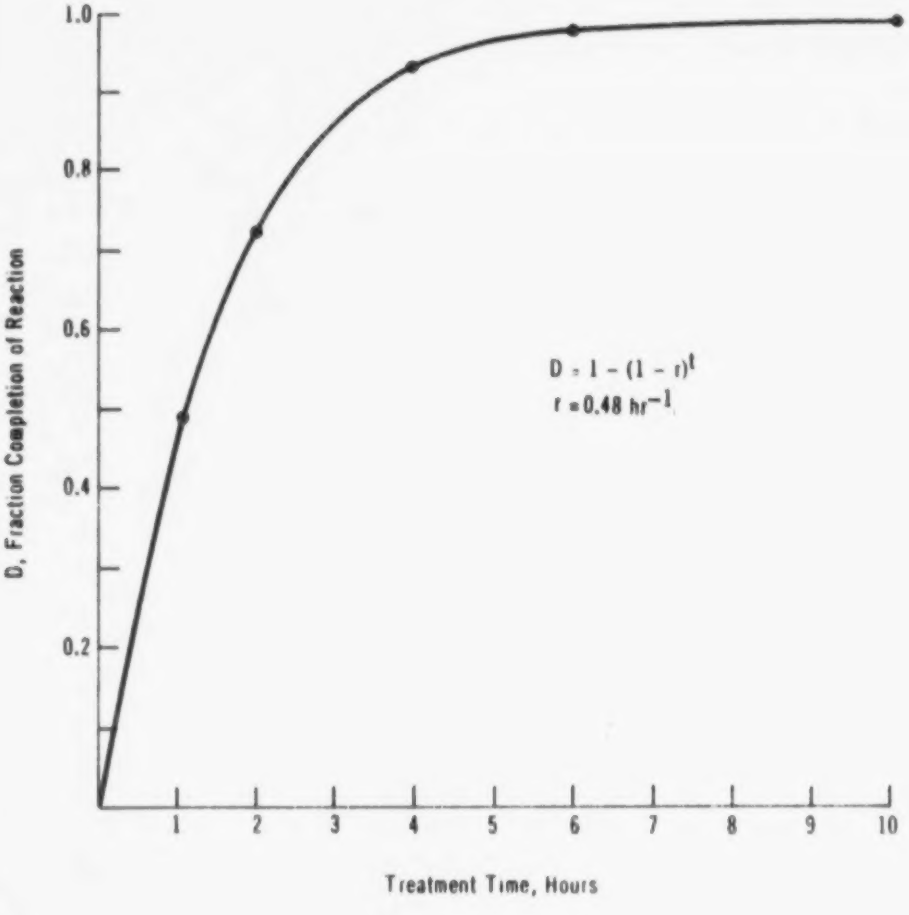
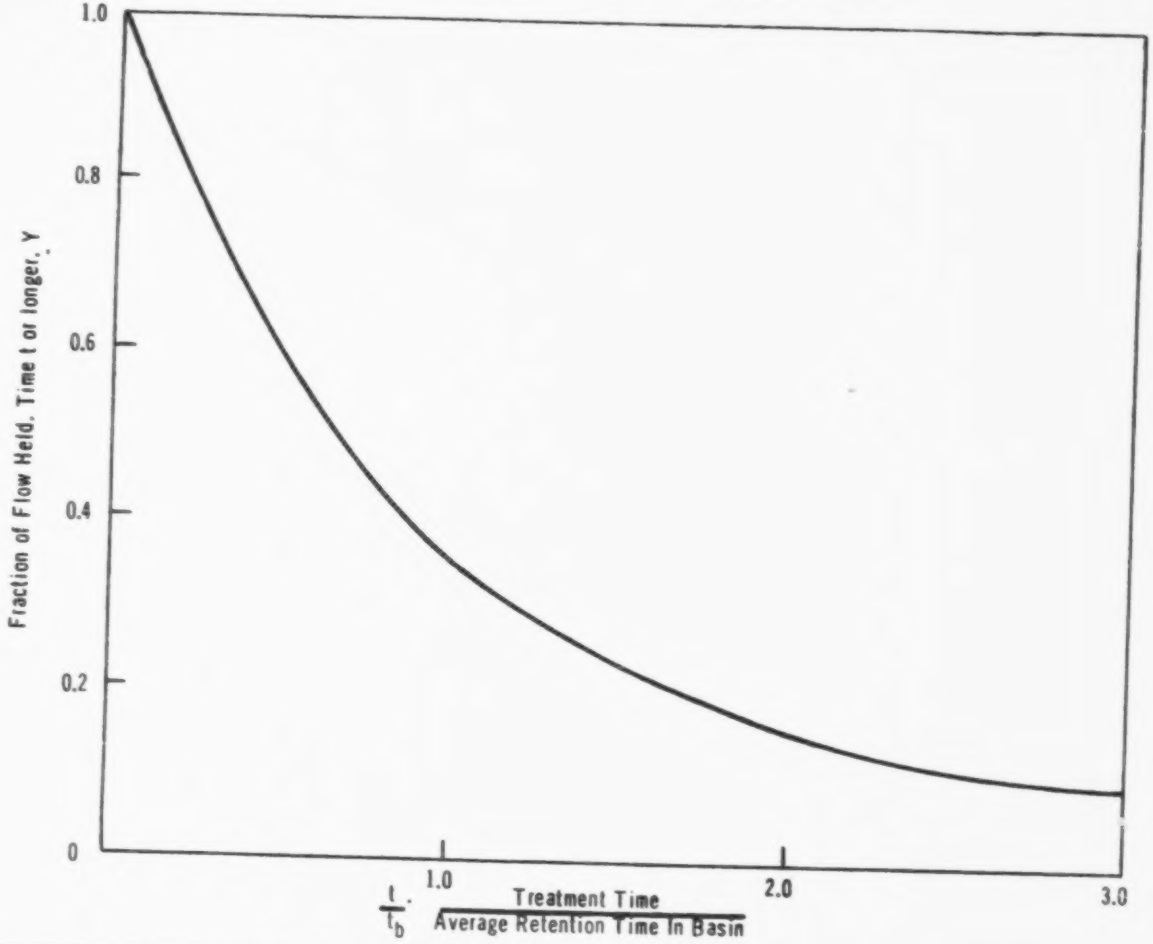


Figure VI–11

COMPLETE MIXING KINETICS IN A SINGLE BASIN



The performance of a continuous system at a residence time of 6 and 12 hours is determined by integrating the values of degree of completion of reaction and the mixing theory data. This is accomplished graphically as shown in Figure VI-12, where the area under the curve, as a fraction of the total area, is a prediction of the efficiency of a continuous system which has the specified retention time.

The results for propylene glycol wastewater treatment, shown in Figure VI-12 predict a removal efficiency of 86% of the TOD at a residence time of 12 hours in a completely mixed single basin. The design of the bench scale continuous units and the pilot plant was based on this information as a starting operating condition.

D. Bench Scale Continuous Units

Two bench scale units were built to determine the removal efficiency of a continuous system. The unit, shown in Figure VI-13, was based on a design adopted from Busch (1963).

Operation was difficult and continuous sampling proved to be impractical. The bench scale continuous units were not operated long enough to obtain equilibrium values or to allow measurement of any design parameters.

The units were operated on a neutralized propylene glycol waste diluted with river water to a 6% NaCl concentration. One unit was seeded with the acclimated mixed culture and the other with Bacterium No. 52. Sampling was done by collecting one liter samples, homogenizing, and returning the unused portion of the sample. The total volume of the substrate, in each unit, was 5.5 liters. The dilution water was gradually reduced until the feed was at full strength.

The residence time (t_o) in the continuous unit can be calculated by the following equation:

$$t_o = \frac{V}{Q} = \frac{C_o - Ct}{\left(\frac{-dc}{dt}\right)_{C_t} M_t}$$

where

V = aeration volume

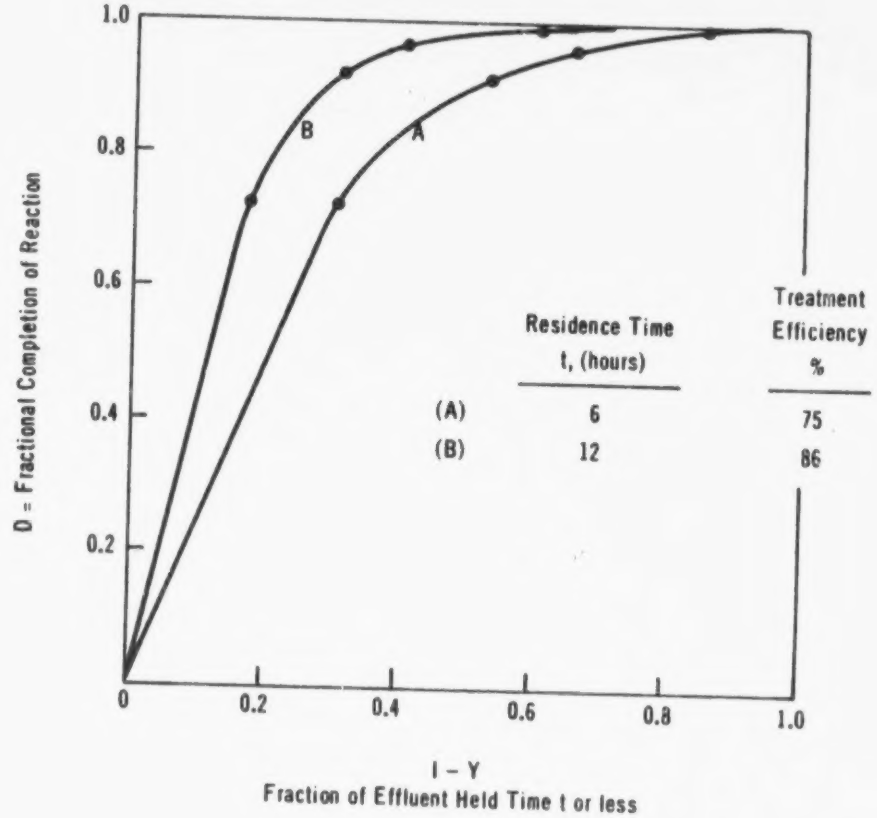
Q = rate of flow

C_o = initial TOD

C_t = effluent TOD

Figure VI-12

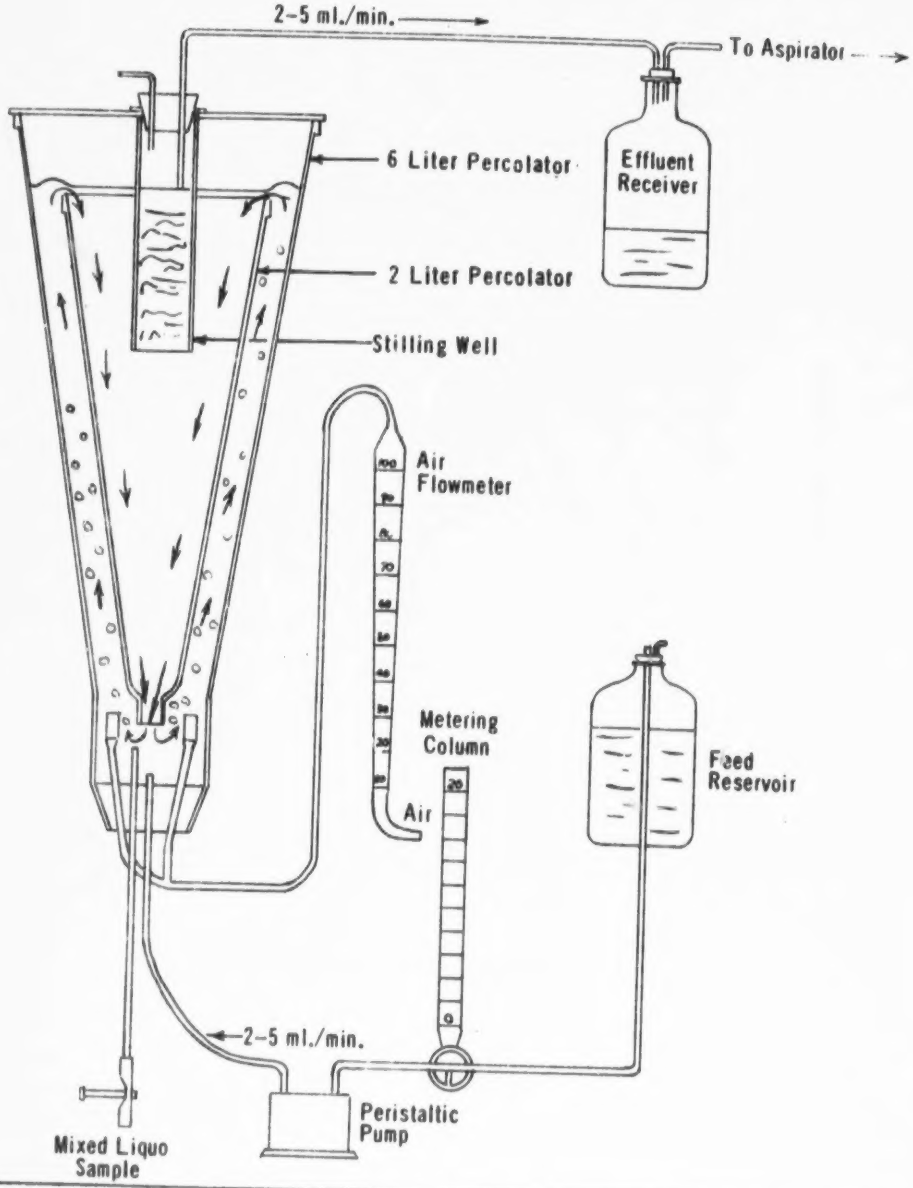
CALCULATED TREATMENT EFFICIENCY OF PROPYLENE GLYCOL IN A CONTINUOUS SYSTEM



	Residence Time t, (hours)	Treatment Efficiency %
(A)	6	75
(B)	12	86

Figure VI-13

BENCH SCALE CONTINUOUS BIO-OXIDATION UNIT



2-5 ml./min.
To Aspirator
6 Liter Percolator
Effluent Receiver
2 Liter Percolator
Stilling Well
Air Flowmeter
100
90
80
70
60
50
40
30
20
10
Air
Metering Column
20
0
Feed Reservoir
2-5 ml./min.
Peristaltic Pump
Mixed Liquo Sample

$(\frac{-dc}{dt})_{C_t M_t}$ = overall reaction rate

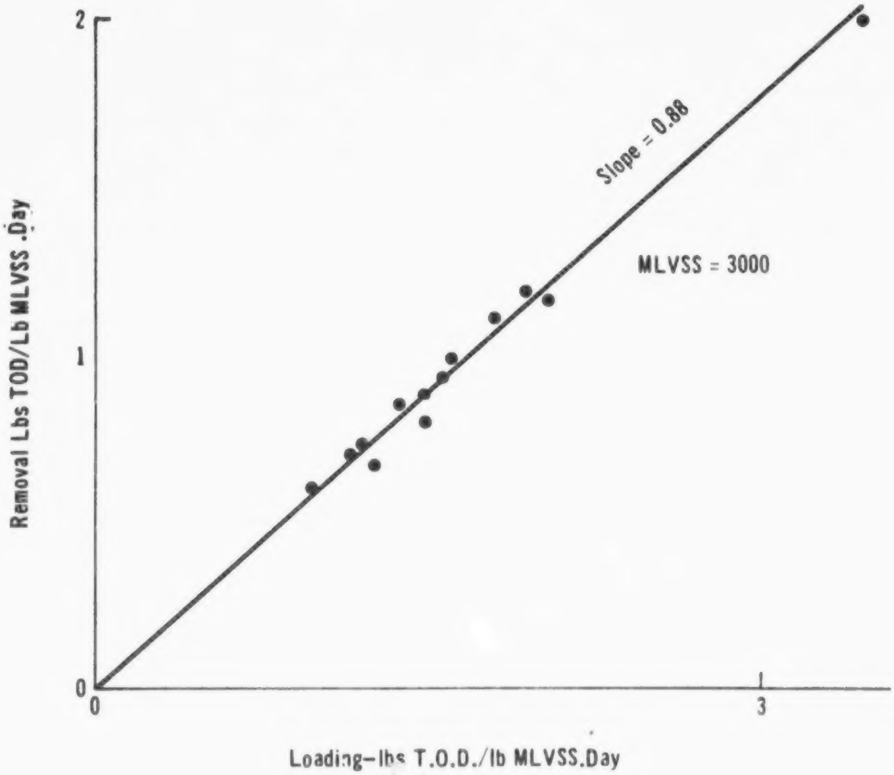
M_t = active mass at time t (MLVSS)

The loading-removal data is plotted in Figure VI-14. At a residence time of 12 hours, a TOD removal of 88% and a filtered effluent quality of 150 ppm. TOD was obtained. The results also indicate, in general, that the loading should be kept below 1.0 pound TOD per pound MLVSS per day, in order to produce an effluent quality of less than 200 ppm. TOD.

The TOD concentration in the turbid effluent from the continuous units averaged about 300 ppm., although it contained no residual organics present in the feed. Preliminary tests indicated that the TOD concentration could be reduced to 100-150 ppm. by chemical flocculation. A chemical flocculation step was, therefore, included in the design of the pilot plant.

Figure VI–14

LOADING–REMOVAL RELATIONSHIP, BENCH SCALE CONTINUOUS UNIT
(Bacterium 52–Propylene glycol–8.5% salt)



SECTION VII

ACTIVATED SLUDGE PILOT PLANT

The preliminary batch tests and the limited tests on bench scale continuous units indicated that glycol waste brines containing up to 10% salt could be successfully biodegraded. The efficiency of TOD removal varied between 85 to 92% and a product of less than 200 ppm. TOD was obtained both from synthetic solutions and samples from the actual wastewater streams. Larger scale testing was required to study the operation under continuous feeding from the production plant, to measure the process parameters under varying conditions of operation, and to obtain accurate engineering design information for economic appraisal. To meet these requirements, an activated sludge pilot plant similar to that described by Mulbarger (1966) was designed and constructed for an average waste flow rate of 0.5 gallons per minute.

A. Plant Description and Operation

A flow diagram of the plant is shown in Figure VII-1. The plant contains the following major components:

1. A cooling tower with a recirculating pump. The basin of the tower has a capacity of 28 gallons.

2. A river water supply line to the cooling tower with a density-controlled automatic valve.

3. An acid tank feeding into the suction line of the recirculating pump through a pH controlled automatic valve.

4. A nutrient solution tank supplying nutrients to the feed through a metering pump.

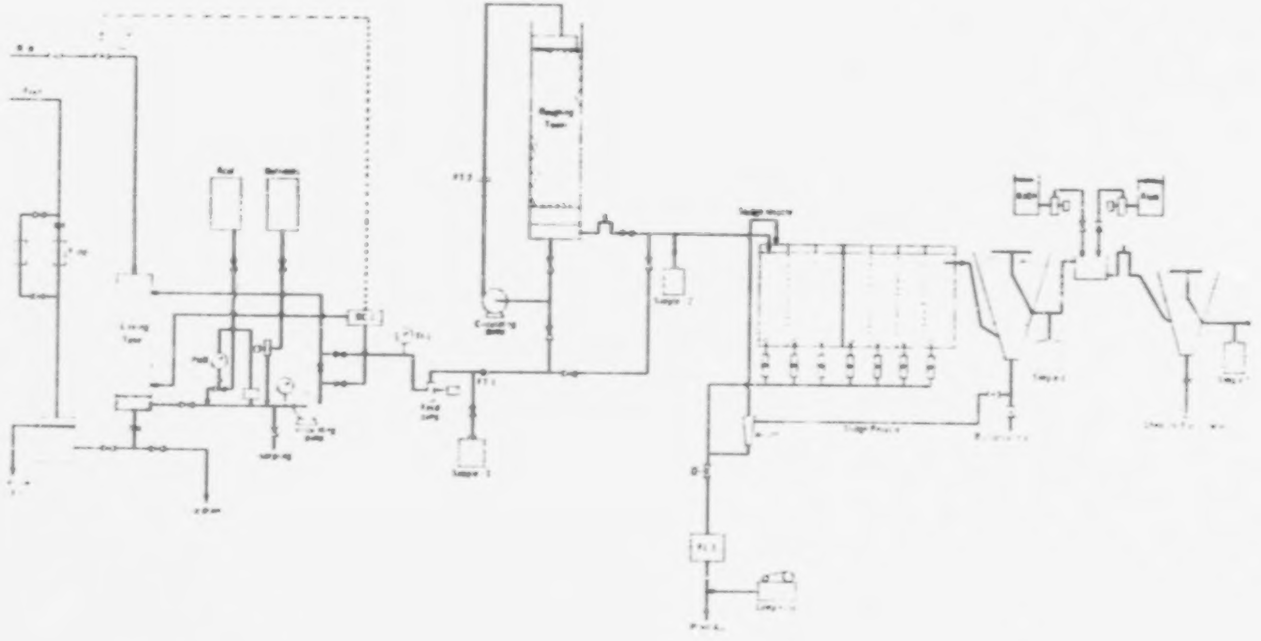
5. A packed Plexiglas roughing column, 18 inches in diameter by 96 inches tall, with its recirculating pump.

6. A 280-gallon aerator tank made of Plexiglas with six removable partitions. Diffused air is introduced into the bottom of each compartment and controlled by needle valves on rotameters.

7. Two 50-gallon Plexiglas settlers, each with an adjustable overflow weir and an airlift to pump the settled solids from the bottom.

Figure V11-1

ACTIVATED SLUDGE MINI PLANT - FLOW DIAGRAM


FT 2
FT 1
Sample 1
Sample 2
Sludge Recycle

8. A 5-gallon glass battery jar with a stirrer and two metering pumps for flocculant mixing.

9. Various composite time-operated samplers.

All components except the cooling tower and the feed lines are mounted on a portable structural steel frame. Figure VII-2 is a photograph showing the aeration tank and the rotameters on the inlets to the air diffusers in the bottom of each compartment. The aeration tank is covered and vented by suction to a water scrubber.

Figure VII-3 shows the first settling tank where the biofloc settles and the two samplers that periodically sample the feed to the aeration tank as well as the overflow from the settling tank. Figure VII-4 shows the flocculation vessel, the metering pumps, and the pH control. This vessel is fed by gravity from the first settler and flows by gravity to the second settler where the alum flocculant is settled.

Plant Operation

The waste stream from the glycol production plant was cooled from 140°F. to a temperature below 100°F. in the cooling tower. The circulation rate over the natural draft spray tower was 25 to 30 gallons per minute. Part of the stream to the tower spray nozzle was diverted to a jet below the liquid level in the tower basin to thoroughly mix the basin contents with the raw feed as it enters. The suction line to the pump operated under a vacuum of 15 to 20 inches of mercury, which lends itself conveniently to the addition and mixing of the nutrients and acid.

Good mixing, both in the basin and in the pump, has been found to be necessary for good pH control, since the alkalinity of the feed varies between 0.05 and 0.4% sodium hydroxide. The neutralization of the feed to a pH of around 7.8 with either a 10% H_2SO_4 solution or, later, with a 38% HCl solution, was controlled by an apparatus that measures and records the pH of the discharge stream from the cooling tower circulating pump. The pH control circuit shuts off the feed to the activated sludge aeration tanks if the pH goes above 8.5 or below 5.5 units.

The nutrient solution, 3.17% $(NH_4)_2SO_4$ and 0.73% K_2HPO_4, is fed into the circulation pump suction line by a Model 2M1 Moyno pump. The rate of addition is controlled to result in the required concentrations of nitrogen and phosphorus in the feed.

Figure VII-2. Aeration Tank

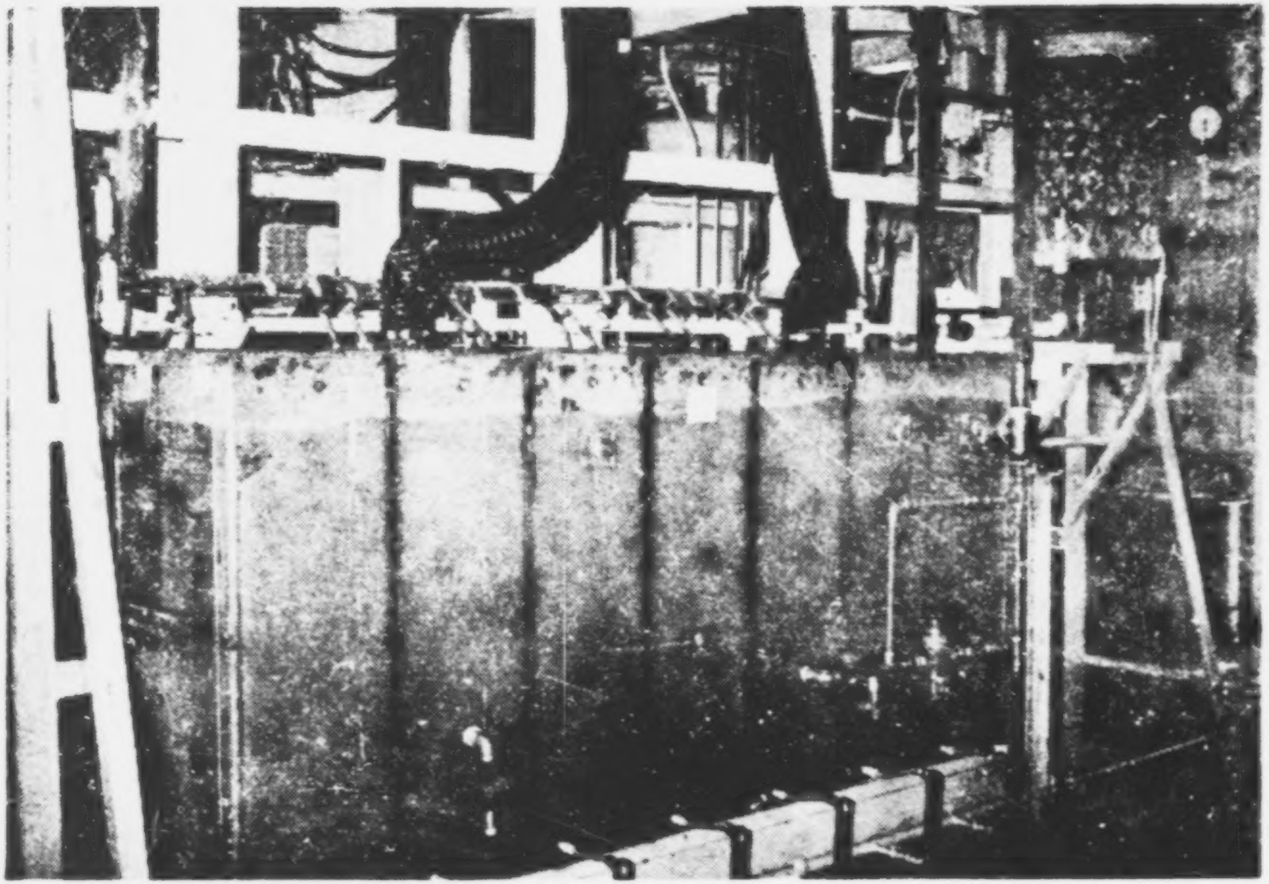


Figure VII-3. First Settling Tank and Composite Samplers

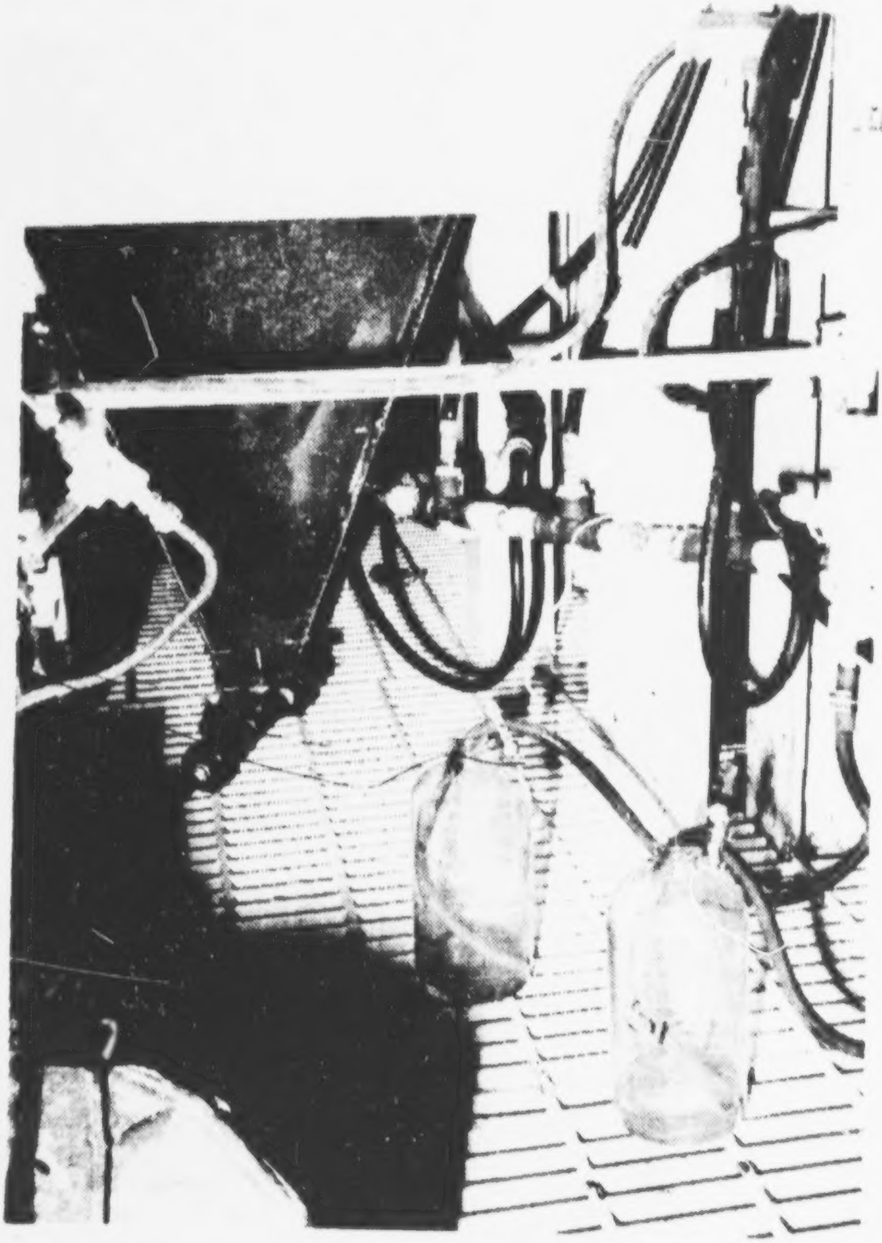
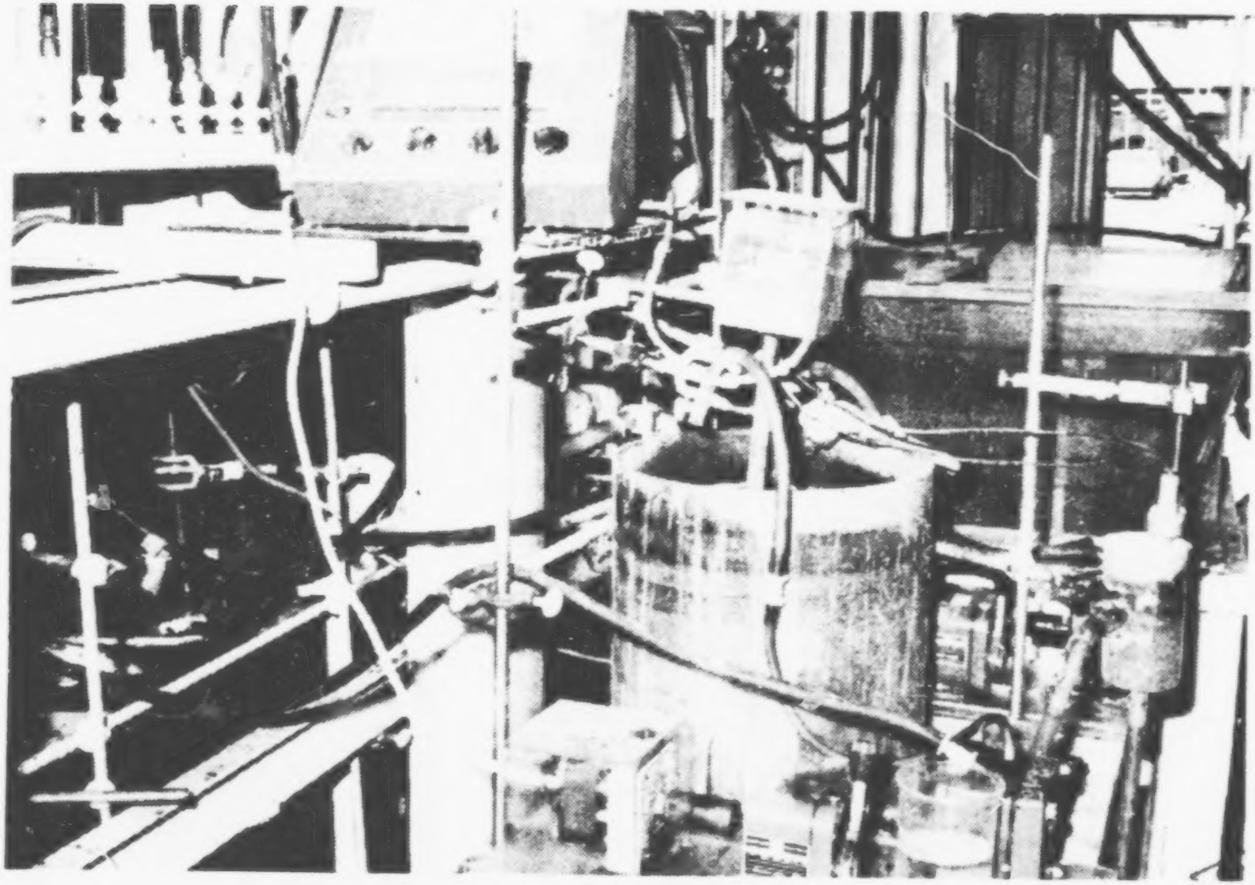


Figure VII-4. Flocculation Vessel With pH Control



Any entrained air had to be separated from the treated feed stream to enable proper functioning of the flow recorders and the density control apparatus. This was achieved by forwarding the circulating pump discharge to an elevated Plexiglas vessel with an 8-inch high dividing plate. The outlet side of the vessel had an overflow near the top, piped to the cooling tower basin, and a port near the bottom from which the treated feed was drawn.

Provision was made for the addition of fresh water to the incoming glycol effluent at the cooling tower during those times when the NaCl content increases excessively beyond 10%--either due to evaporation or to operational changes. The salt concentration was controlled by the density of the feed. A sample stream from the air separator vessel was piped into the bottom end of a 2-inch vertical pipe 10 feet tall, flanged at its lower end to a 2-inch tee. The stream rose through the pipe and overflowed at a constant level into a plastic pan and drained into the cooling tower. The pressure at the bottom of the column varied with the density of the fluid and was measured by a differential pressure transmitter and recorded as density. The sensitivity of the signal from the transmitter was improved by balancing the column pressure against a fixed column of mercury while the unit was filled with pure water. The transmitter signal is also applied to a pneumatic relay which controls a diaphragm valve on the fresh water supply line to the top of the cooling tower.

The pre-treated feed was forwarded from the air separator either to the roughing tower or to the aeration tank by a metering gear pump (Model 1L2 Moyno) which is adjusted for flow rates from 0.2 to 0.6 gpm.

The roughing column was packed with 5 feet of porcelain Berl saddles. A recycle pump was adjusted to give a rate of recycle five to ten times that of the feed flow rate. The column was started by recycling about 15 gallons of acclimated culture and feeding with glycol daily for a period of two weeks to build up the bacteria on the packing. Then the column was switched onto the continuous feed. The overflow of the column basin flowed by gravity to the aeration tank.

Prior to start up, a batch of 400 gallons of the mixed culture was acclimated to the glycol effluent in a glass tank equipped with air diffusers. This batch-grown culture was used to fill the aeration tank and was kept growing by a fill-and-draw procedure as a standby bacterial supply.

The diffused air to the aeration tank was supplied from a header, at 8 psig, at a rate of 1.5 cfm to each of seven diffusers. The total air supply, 10.5 cfm, was about 0.33 cfm per cubic foot of aerator volume.

The mixed liquor overflowing from the aerator entered the first settling tank through an inlet port about 15 inches above the bottom. The settled sludge was returned to the feed end of the aerator by means of an air lift pump operated by a timer adjusted to keep the same concentration of suspended solids in the aeration tank. The overflow from the first settler was usually slightly turbid. It flows into the flocculator where alum and caustic solutions are added, then to the second settling tank.

Automatic composite samplers were used to collect samples from the treated feed before and after the roughing column and from the overflow of the first and second settling tanks. The timer-operated samplers collect 1 to 2 milliliters at 15-minute intervals. Samples of the wastes, after the biological treatment, were collected in bottles kept cool in dry ice to prevent any further biological action. The 24-hour composite samples were analyzed daily for TOD, glycols and other components, percent NaCl, pH and nutrients. A sample of the mixed liquor in the aeration tank was collected daily for determination of the suspended solids.

B. Evaluation of the Roughing Column

A film of bacterial growth was built up on the surface of the packing in the roughing column by batch feeding the column with propylene glycol. During the period when the plant operation was operating on a mixed ethylene and propylene glycol waste, the feed was directed through the roughing column. Composite samples before and after the column were analyzed daily.

The results of two weeks of operation were erratic. The non-filtered samples from the roughing treatment showed an increase in TOD value, but the initial dissolved organics, ethylene and propylene glycol were always reduced.

The operation of the packed column without additional air was found to be oxygen limited and the bacterial film became anaerobic as the bacteria increased on the packing. The packing turned black in less than ten days of operation. A diffuser was installed at the bottom of the column, and air was supplied, under a pressure of about 2 atmosphere, at a rate of 2 cubic feed per minute. The column was then successfully operated for a period of three weeks, with no indication of anaerobic conditions developing. The flow rate of 0.4 gpm corresponds to about a 1 hour residence time in the column at a recycle ratio of 1:20. The results are presented in Table VII-1. A TOD removal of over 30% was obtained except during period when the air diffuser was plugged. Cleaning the air diffuser improved the operation of the column overnight.

TABLE VII-1

OPERATION OF THE ROUGHING COLUMN WITH FORCED DRAFT AIR

	Pretreated Feed		Effluent from Column			
Date	PG ppm	TOD ppm	PG ppm	TOD ppm	TOD Removal %	Flow Rate gals./min.
11-27	520	1750	150	1040	40.6	0.32
11-28	260	1680	-	1120	33.4	0.32
11-29	300	1280	-	830	35.1	0.32
11-30	230	1420	-	870	38.7	0.32
12-1	220	1130	-	930	17.7	0.36
12-2	650	1300	360	1040	20.0	0.36
12-3	510	1760	310	1640	6.8[1]	0.40
12-4	520	1490	190	1030	30.8	0.40
12-5	500	1490	180	1290	13.4[1]	0.40
12-6	350	1260	140	950	24.6	0.40
12-7	570	1590	260	1170	26.4	0.40
12-8	470	1280	290	1090	14.9[1]	0.40
12-9	530	1230	330	710	42.2	0.40
12-10	280	1240	250	1030	17.0[1]	0.40
12-11	560	1220	270	510	58.0	0.40
12-13	660	1200	420	750	37.5	0.40

[1] Air diffuser at bottom of column was plugged with a fine material that does not resemble the bacteria. When cleaned, the removal of TOD improved overnight.

C. Results of Different Modes of Operation

The operation of the pilot plant as a plug flow reactor and a completely mixed single basin with a feed composition as obtained from the glycol production plant constituted the modes of operation studied. The objective was to determine the minimum residence time required for the complete oxidation of the organics components of the feed under the varying conditions of loading. The results obtained under the several modes of operation are presented and discussed under the following subsections. The detailed daily records of the plant operation are presented in Appendix B.

Mixed Ethylene and Propylene Glycol Wastewaters Plug Flow Operation

The activated sludge pilot plant was started with a bacterial culture grown batchwise in a 300 gallon glass tank filled daily with pretreated glycol wastewater. During the period of operation, from June 24 to August 26, 1970, partitions were placed in the aeration tank. A dye study showed that the configuration of the aeration tank was that of a plug flow reactor with seven completely mixed reactors in series.

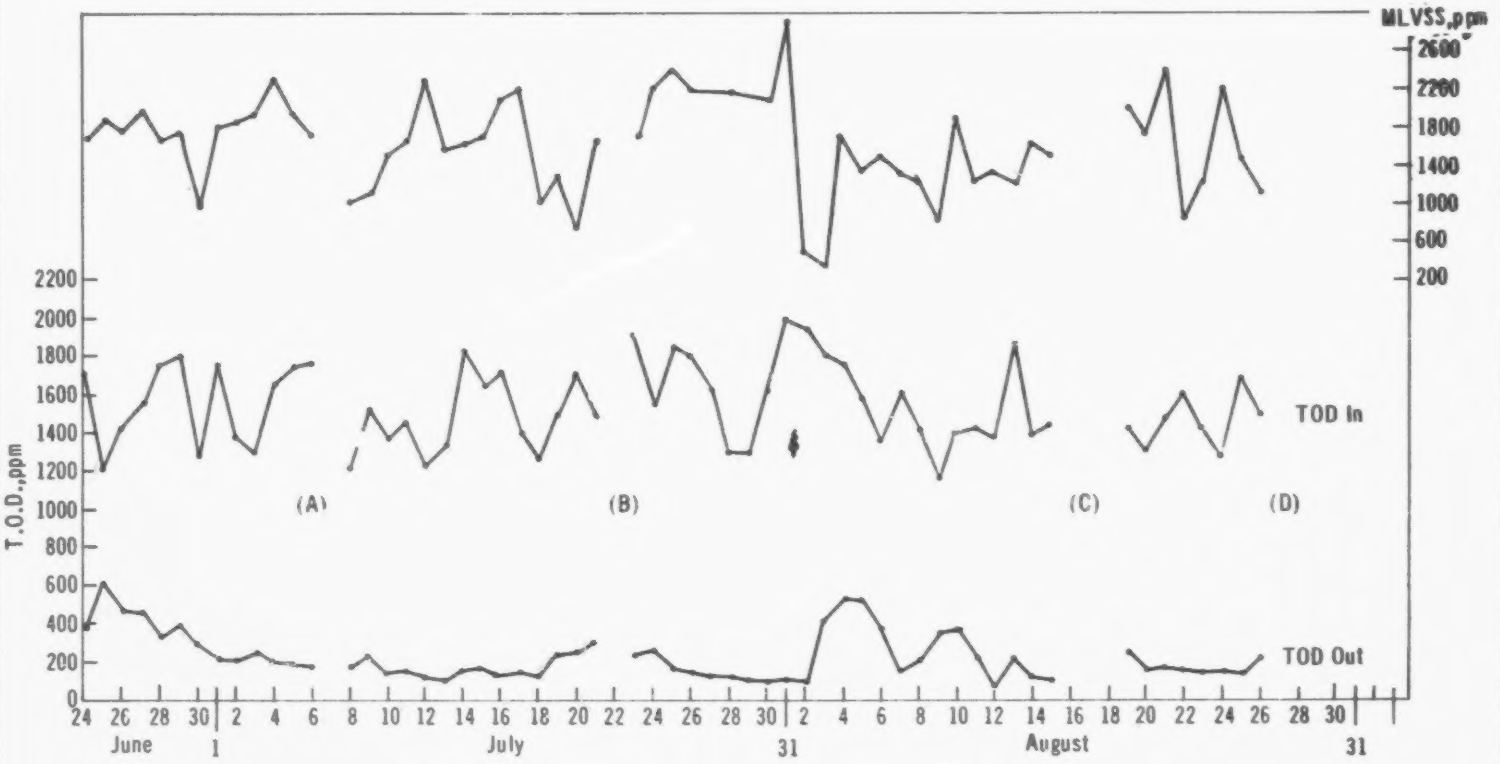
The feed was a mixture containing about one third ethylene glycol and two thirds propylene glycol. The TOD of the feed varied between 1200 to 2000 ppm. The flow rate of the feed was brought up gradually to 0.3 gpm, corresponding to a residence time of 14 hours in the aeration tank. The removal of TOD varied between 86 to 95% at this flow rate, yielding a product quality between 100 and 230 ppm. TOD. When the feed was switched over to propylene glycol waste for a period of five days (July 31 to August 4), a higher percent removal, 90 to 95%, and a product of less than a 100 ppm. TOD was obtained. Due to mechanical difficulties with the feed pump, the feed was then switched back to the mixed waste stream.

A plot of the TOD, in and out, and the concentration of MLVSS in the aeration tank over this operating period, is shown in Figure VII-5. A complete daily record of the analyses is given in Table XI-2 of Appendix B.

On August 22 the feed rate was increased to 0.4 gpm (giving a residence time of about 10 hours). Good operation was maintained for three days at this higher flow rate, with TOD removal of 88 to 91%. As the TOD concentration in the feed increased, residual glycol and higher TOD were produced in the treated waste. The sludge settling became less efficient and it became difficult to maintain a MLSS over 100 ppm.

Figure VII–5

PILOT PLANT OPERATION
MIXED PROPYLENE AND ETHYLENE GLYCOLS WASTEWATER
(Plug flow operation)



During the interruptions of the operation (A, B, C and D in Figure VII-5) the aeration tank was either fed propylene glycol or secondary culture was added before startup. Usually the batch grown bacteria suffered a decrease in concentration when exposed to continuous flow conditions, followed by a culture increase and better settling characteristics, as the bacteria became acclimated to the flow conditions.

A schematic of the operation showing the range of the results obtained during ten days of continuous operation at a flow rate of 0.3 gpm is shown in Figure VII-6. During this period the roughing column was in operation most of the time. The loading-removal relationship obtained during this period is shown in Figure VII-7. The indicated slope of 0.834 corresponds very well with the calculated value from batch tests for a residence time of 12 hours. The effluent-loading relationship is presented in Figure VII-8. An effluent quality below 200 ppm. TOD can be obtained at a loading of up to 2.0 pounds TOD per pound MLVSS per day in this mode of operation.

Propylene Glycol Waste - Completely Mixed Reactor

The partitions were removed from the aeration tank, and the feed was switched to wastes containing only propylene glycol. A hydrochloric acid (38%) rubber lined tank was installed and HCl used for neutralization.

The feed to the completely mixed aeration tanks was started on July 9, at a rate of 0.325 gpm (12.8 hours residence time). For the first week of operation the MLVSS remained low and the feed had a high TOD concentration. This high loading resulted in only 70 to 77% removal of TOD with the product containing higher concentrations of TOD and propylene glycol. From September 24 to October 2, a TOD removal of over 90% was obtained and the MLVSS was building up, while the TOD in the feed varied from 1940 to 2400 ppm.

On October 3, the temperature of the feed rose to 46°C, due to the plugging of the spray nozzle in the cooling tower. This was accompanied by an increase of TOD in the feed to 3240 ppm. The bacteria were killed, anaerobic conditions developed, and the bacteria were lost by floating and carryover. For a period of two weeks following this incident, it was difficult to build up the concentration of the bacteria. The settling of the sludge was very inferior and most of the bacteria were filamentous in nature.

From October 20 to October 27, 88% to 94% TOD removal was obtained and the sludge settling improved as the bacterial concentration built up to 1660 ppm. The TOD in the feed then began to fluctuate to very high concentrations, again

Figure VII–6

ACTIVATED SLUDGE PILOT PLANT OPERATION

Plug Flow–Mixed Ethylene Glycol and Propylene Glycol Wastewater.

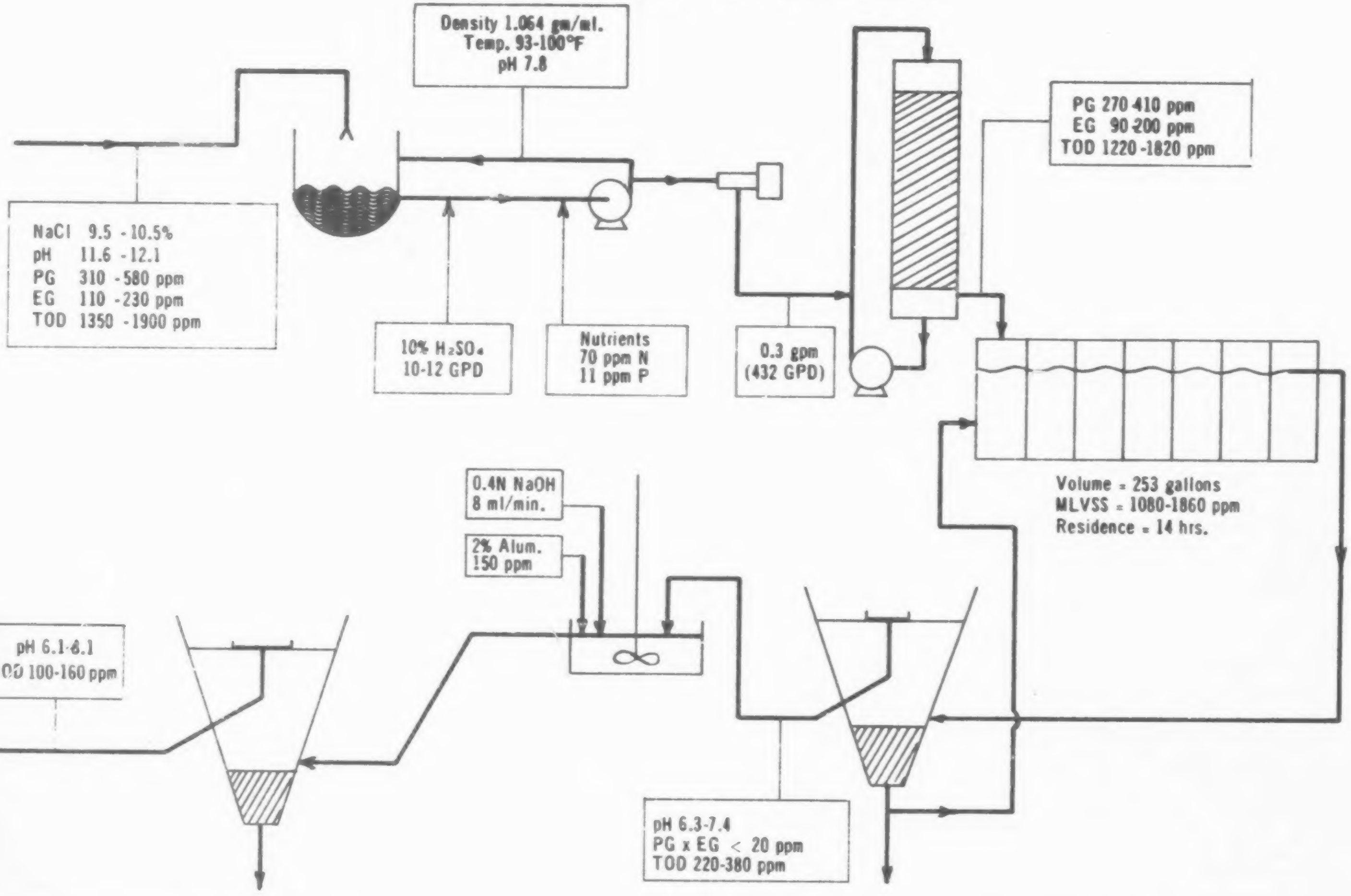

Density 1.064 gm/ml.
Temp. 93-100°F
pH 7.8
NaCl 9.5 - 10.5%
pH 11.6 - 12.1
PG 310 - 580 ppm
EG 110 - 230 ppm
TOD 1350 - 1900 ppm
10% H₂SO₄
10-12 GPD
Nutrients
70 ppm N
11 ppm P
0.3 gpm
(432 GPD)
PG 270-410 ppm
EG 90-200 ppm
TOD 1220-1820 ppm
Volume = 253 gallons
MLVSS = 1080-1860 ppm
Residence = 14 hrs.
0.4N NaOH
8 ml/min.
2% Alum.
150 ppm
pH 6.1-8.1
TOD 100-160 ppm
pH 6.3-7.4
PG x EG < 20 ppm
TOD 220-380 ppm

Figure VII-7
LOADING REMOVAL CURVE
PLUG FLOW – MIXED ETHYLENE GLYCOL AND PROPYLENE GLYCOL WASTEWATER

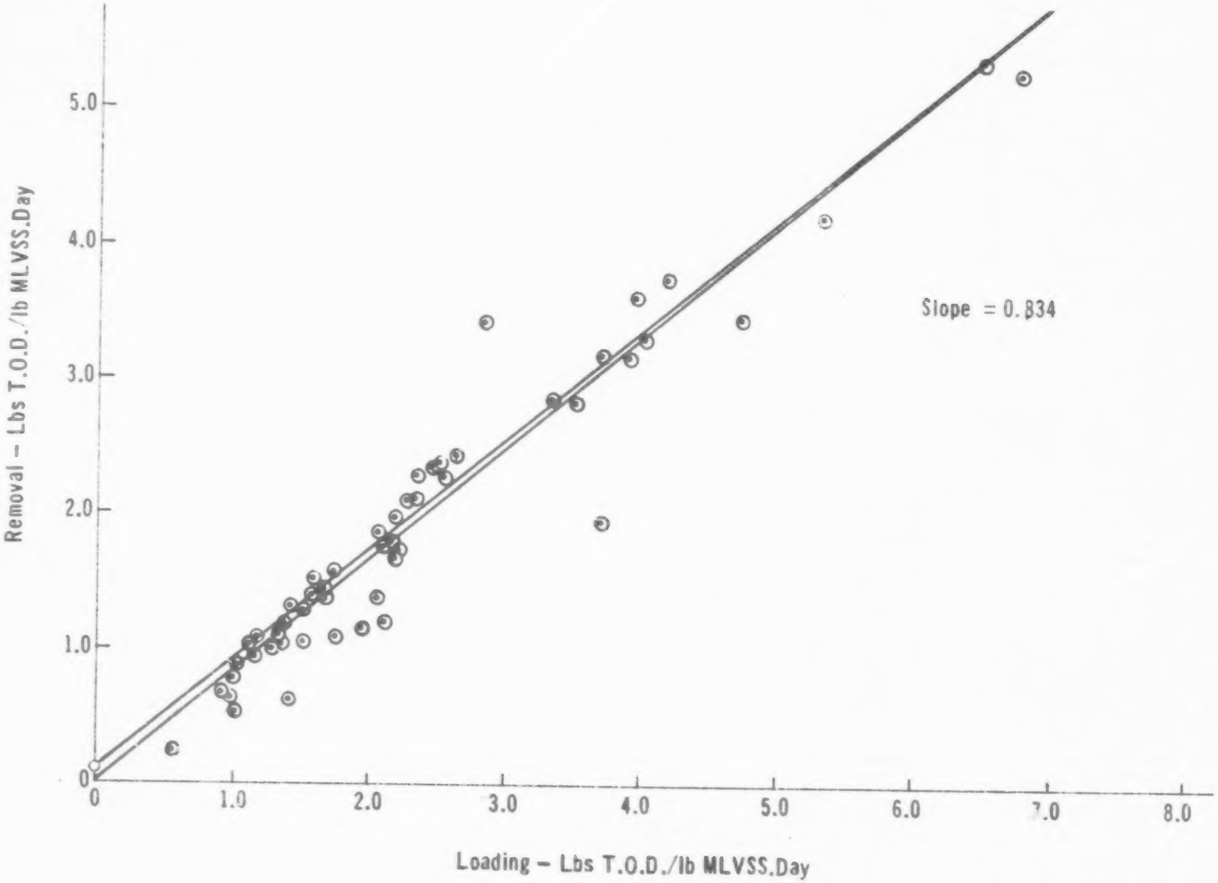
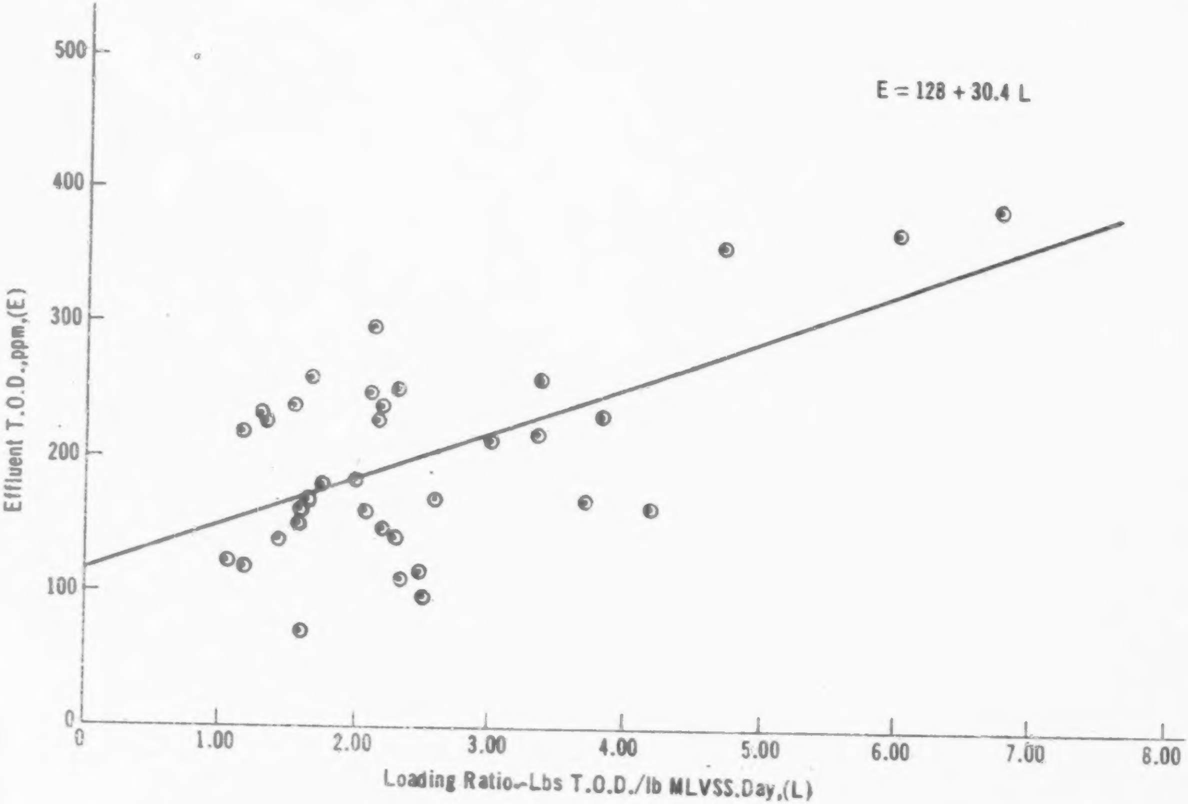


Figure VII-8

EFFLUENT LOADING CURVE

PLUG FLOW – MIXED ETHYLENE GLYCOL AND PROPYLENE GLYCOL WASTEWATER



accompanied by a loss of the bacterial concentration. It was decided to install a 3000-gallon tank in the feed system to equalize the organic loading to the activated sludge plant, to maintain a near steady state operation. The results of this period of operation are plotted in Figure VII-9. The complete daily analyses are given in Table XI-3 of Appendix B.

Equalized Propylene Glycol Waste Completely Mixed Reactor

The feed was switched to a propylene glycol waste stream collected from several production trains and was equalized in a 3000-gallon tank before feeding to the pilot plant. A residence time of about 3.5 days in the equalizing tank after neutralization resulted in considerable dampening of the fluctuations in the TOD concentrations. The nutrients were added to the feed after equalization. Addition of the nutrients prior to the tank resulted in the development of anaerobic activity inside the tank. The pilot plant results during November and December, 1970 are plotted in Figure VII-10. The daily analyses are shown in Table XI-4 of Appendix B. The initial flow rate of the feed was 0.32 gpm. It was increased to 0.4 gpm (10.5 hours residence time) in two weeks. Removal efficiencies of over 80% and a product of less than 300 ppm. TOD was obtained during most of this time. Lower removal efficiencies were experienced during this period due to the lowered waste temperatures (60 to 70°F.). Heating the feed to 85°F. resulted in increased activity.

The operation of the activated sludge pilot plant continued through January and February under steady state conditions using equalized feed. The obtained results are given in Table XI-5, Appendix B, and in Figure VII-11. The feed rate was increased to 0.45 gpm on January 26, giving a residence time of 8.25 hours in the aeration basin. The loading and removal relationship is plotted in Figure VII-12, for the period from January 15 to February 22. A removal efficiency of 92% was obtained for loadings between 1.5 to 3.0 pounds TOD per pound of MLVSS per day. The lower end of the loading was found to be operationally critical. At loadings below 1.5, the food to bacteria ratio was too low to maintain the mixed culture in the aeration basin, and resulted in a sudden loss of the bacterial concentration due to endogenous respiration.

D. Operational and Design Parameters

The operation of the activated sludge pilot plant was maintained at nearly steady state during the months of January and February, 1971. The emphasis during this period was on collection of the data necessary for process design. The

Figure VII-9
PILOT PLANT OPERATION
PROPYLENE GLYCOL WASTE – COMPLETELY MIXED REACTOR

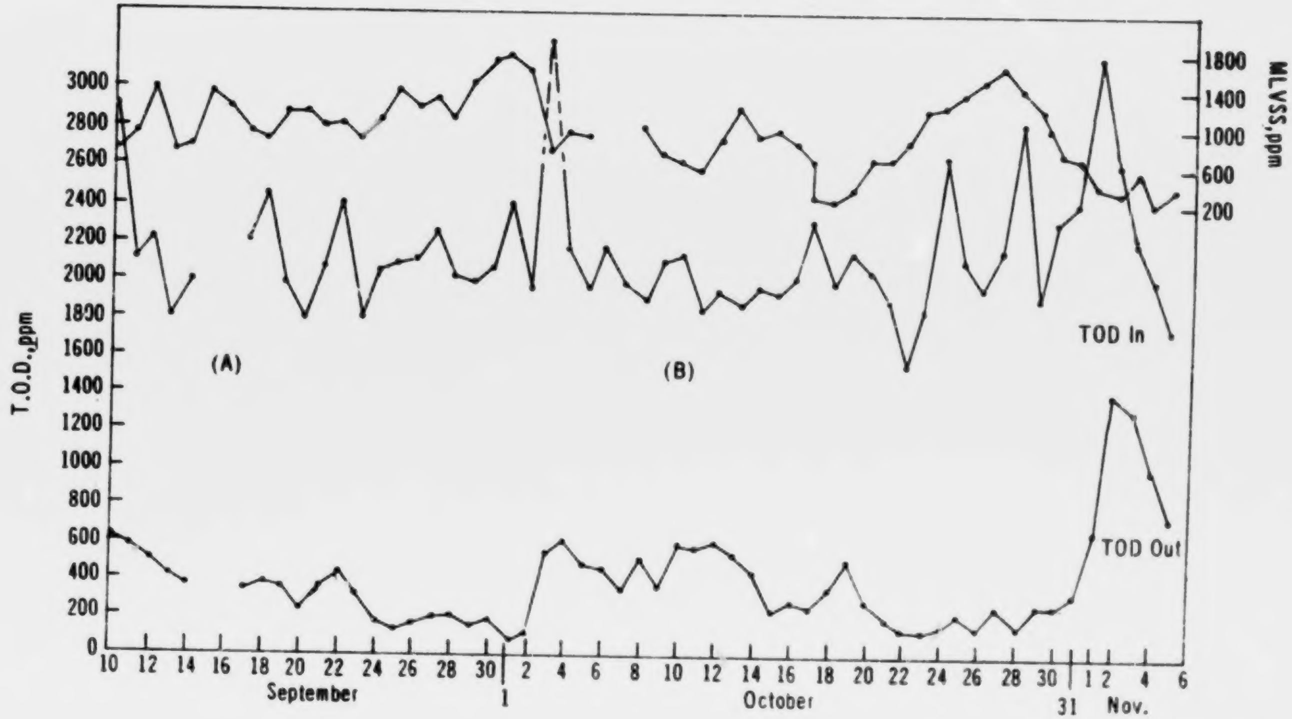


Figure VII-10

PILOT PLANT OPERATION

EQUALIZED PROPYLENE GLYCOL WASTE – COMPLETELY MIXED REACTOR

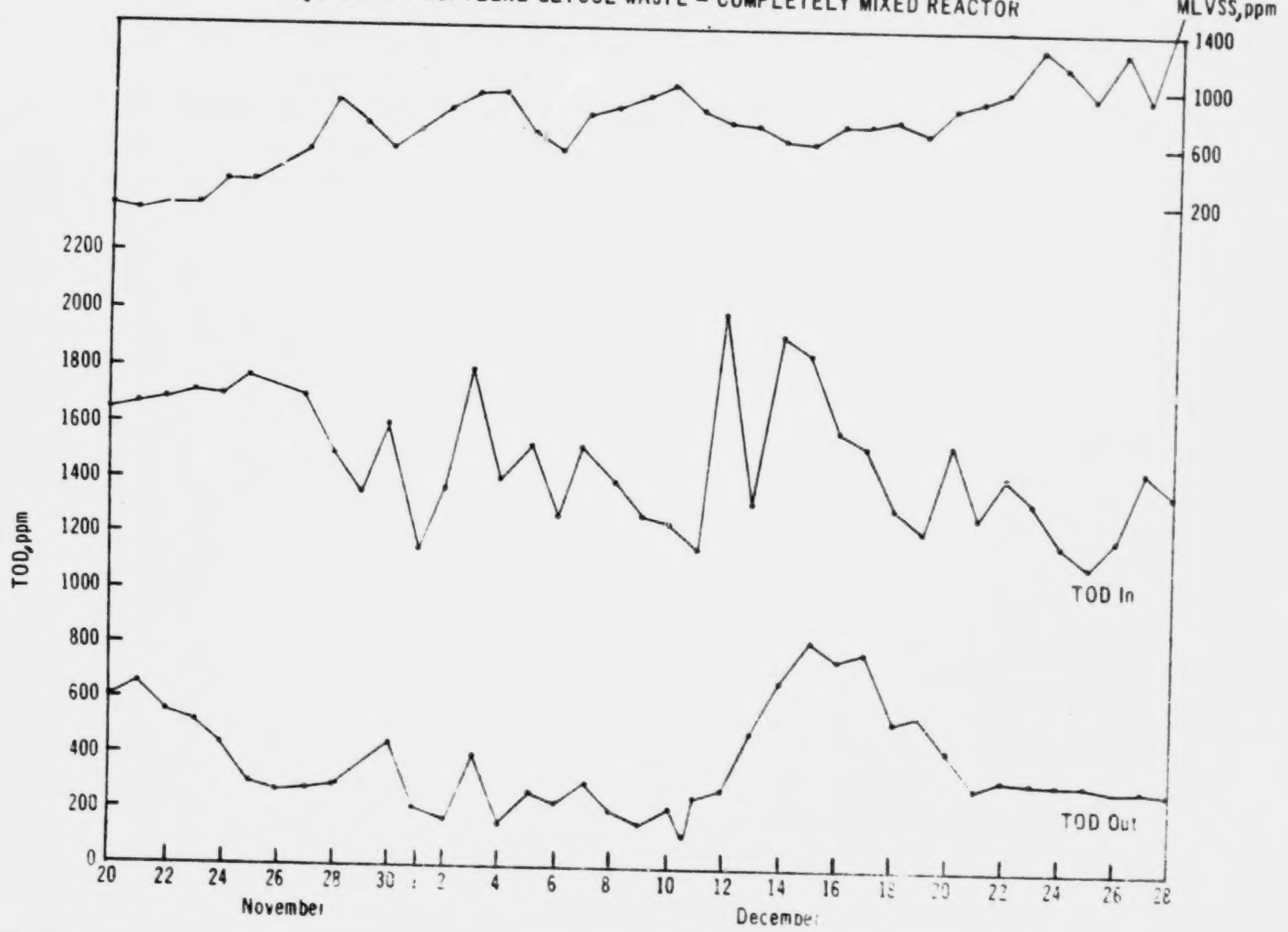


Figure VII-11

PILOT PLANT OPERATION - EQUALIZED PROPYLENE GLYCOL WASTE

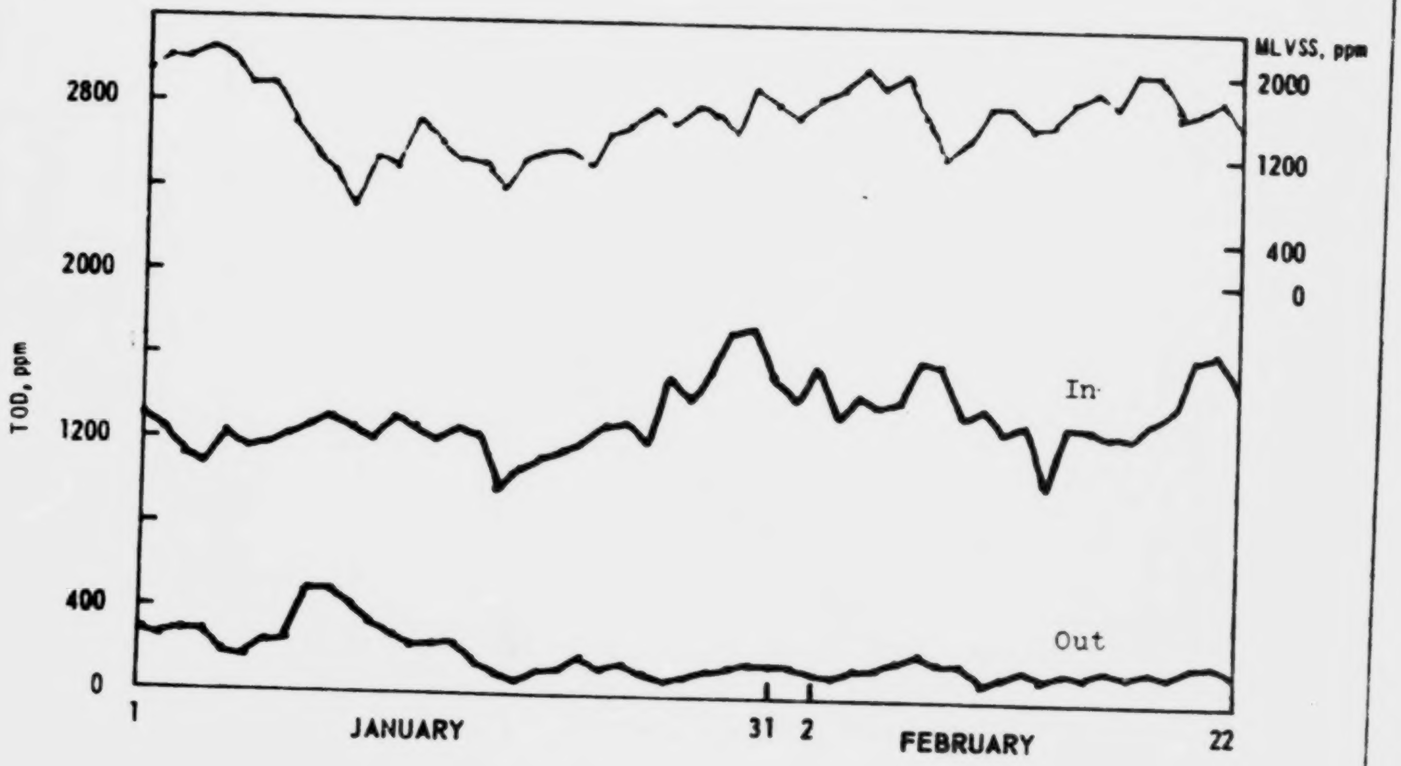
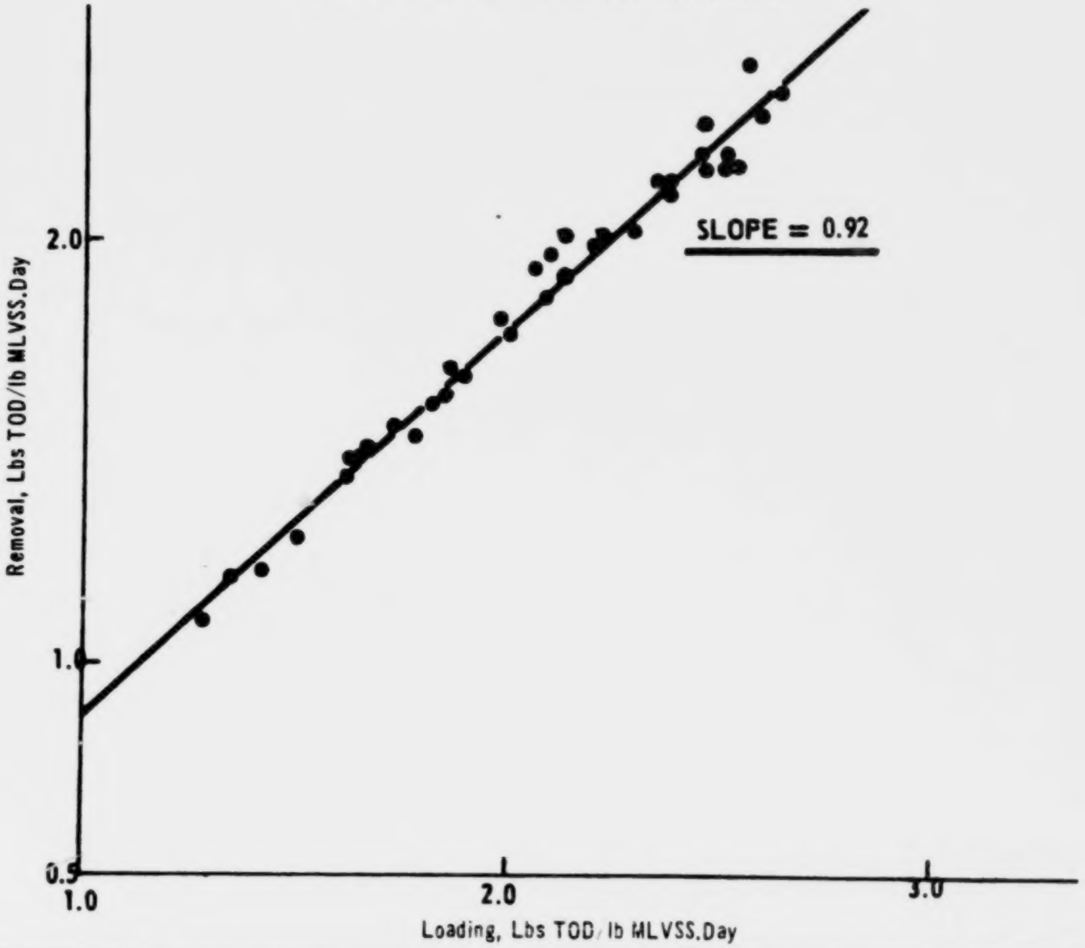


Figure VII-12

LOADING–REMOVAL CURVE
EQUALIZED PROPYLENE GLYCOL WASTEWATER



operational and design parameters of the process are best discussed under the following headings.

Stability of the Biota to Transients

Equalization of the wastewater feed to the aeration basin was found to be necessary to dampen the fluctuations of the organic loading of the activated sludge. Loadings below 1.5 pounds TOD per pound MLVSS per day, resulted in a sudden loss of the bacterial concentration, while at loadings over 4.0 or 5.0 filamentous bacterial growth resulted, with poor settling properties and a resultant high concentration of suspended solids in the effluent from the settling tank. The recommended range of organic loading of this particular culture is 1.5 to 3.0 pounds of TOD per pound of MLVSS per day.

The characteristics of the various components in this culture are given in Appendix C. Biochemical test reactions of forty-eight isolates from the activated sludge indicated that there are no more than 3 or 4 species. The most numerous bacterium is a Gram negative, non-motile, oxidase positive rod.

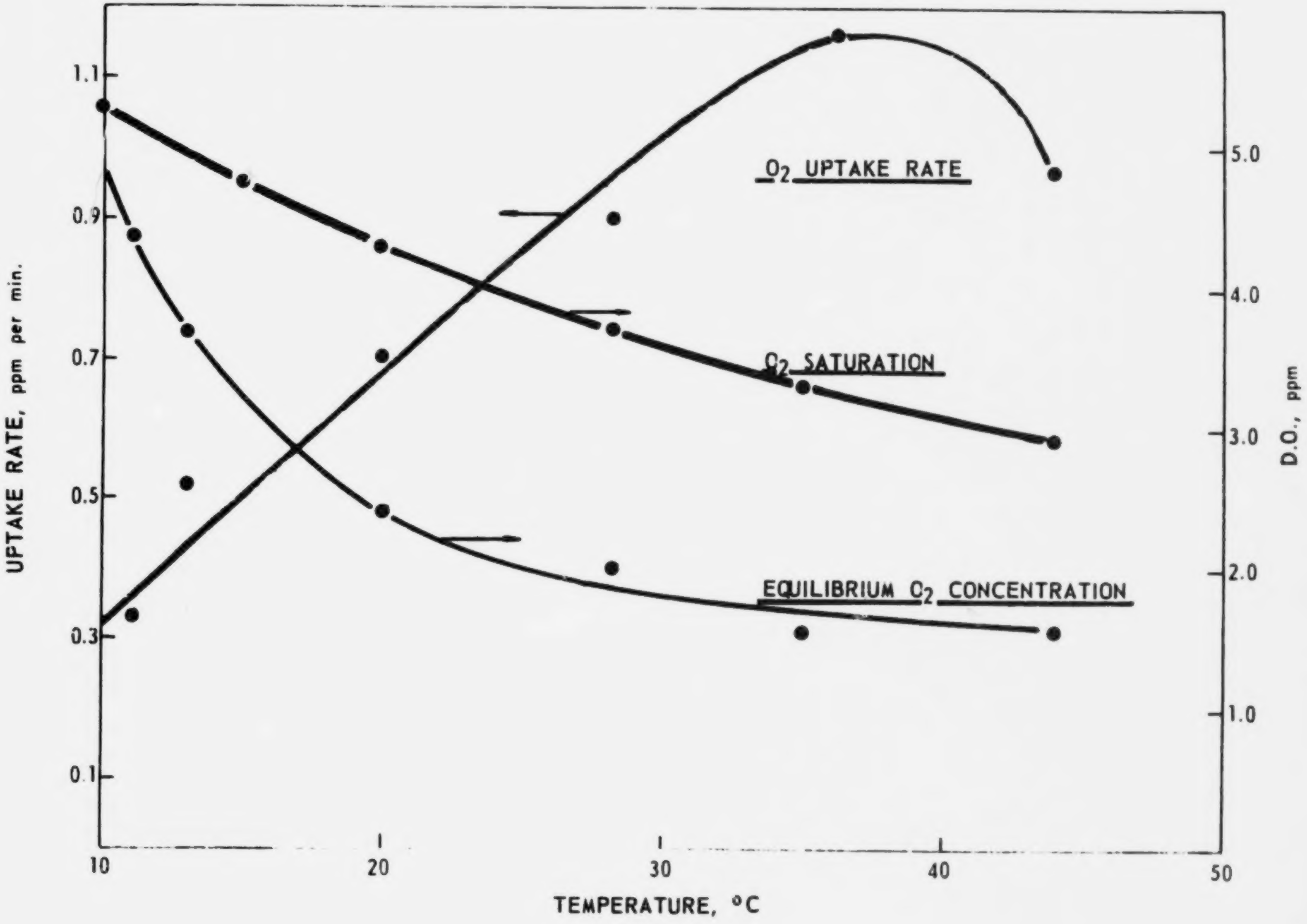
The growth of this culture is favored at higher temperatures. Good operation was maintained during the summer months, at 100°F., but difficulties were encountered at temperatures below 65°F., during the period January 7 to January 13, as indicated in Figure VII-11. The temperature of the aeration basin was maintained at 85°F. by heating the feed during the period from January 14 to the end of February.

The temperature limits were determined in the laboratory continuous unit shown in Figure VII-16. The unit was filled daily with mixed liquor from the pilot plant and loaded with pretreated feed at approximately the same rate as the pilot plant. The temperature of the aeration vessel was varied between 10°C. and 50°C. The oxygen uptake rate under loading, the removal efficiency and sludge production were measured during a 24-hour period.

In Figure VII-13, oxygen saturation, oxygen equilibrium concentration and oxygen uptake rate are plotted as functions of temperature. At 11°C. the oxygen uptake rate decreased to one-third of the value at 20°C., there was no sludge production and the removal efficiency dropped off and residual glycol appeared in the effluent. The bacterial culture formed dense clumps and was difficult to mix with the feed. At temperatures over 40°C., some decrease in oxygen uptake rate was noted, but removal efficiency and sludge production was not affected. The optimum oxygen uptake appears to be at a temperature between 30 and 35°C. (85 to 95°C.).

Figure VII-13

EFFECT OF TEMPERATURE ON UPTAKE RATE



Substrate Removal Rate

For the period of operation from November 20, 1970 to February 28, 1971, the recycle ratio, to the completely mixed aeration tank, was varied between 15 and 25% of the equalized propylene glycol waste feed rate. In Figure VII-14, the effluent TOD is plotted as a function of loading. The initial loading of the aeration tank (TOD_i) is calculated as a weight average of the feed and recycle:

$$TOD_i = \frac{TOD_f + (\text{recycle ratio})\ (TOD_e)}{1 + \text{recycle ratio}} \qquad \text{-----}\ (a)$$

where

TOD_f = Total oxygen demand in the feed.

TOD_e = Total oxygen demand in the effluent.

The line of best fit of the data is represented by:

$$TOD_e = 9.3 + 69.7\ \left(\frac{TOD_i}{t \times MLVSS}\right) \qquad \text{-----}\ (b)$$

The same data can also be presented as in Figure VII-15, where the rate is plotted as a function of a loading ratio. The correlation is given by:

$$R = \frac{TOD_i - TOD_e}{t \times TOD_e} = 1.33 - 0.412\ \frac{TOD_i}{MLVSS} \qquad \text{-----}\ (c)$$

The coefficients of correlation for equations (b) and (c) are 0.725 and 0.816, respectively. Both relations can be used to calculate the residence time (t) and the volume of the reaction basin required.

Oxygen Utilization Rate

The laboratory activated sludge unit, used for oxygen measurements, is shown in Figure VII-16. The aerator (4.1 liters) was started daily with mixed liquor obtained from the pilot plant, and air was supplied to it at a rate of 600 ml./min.

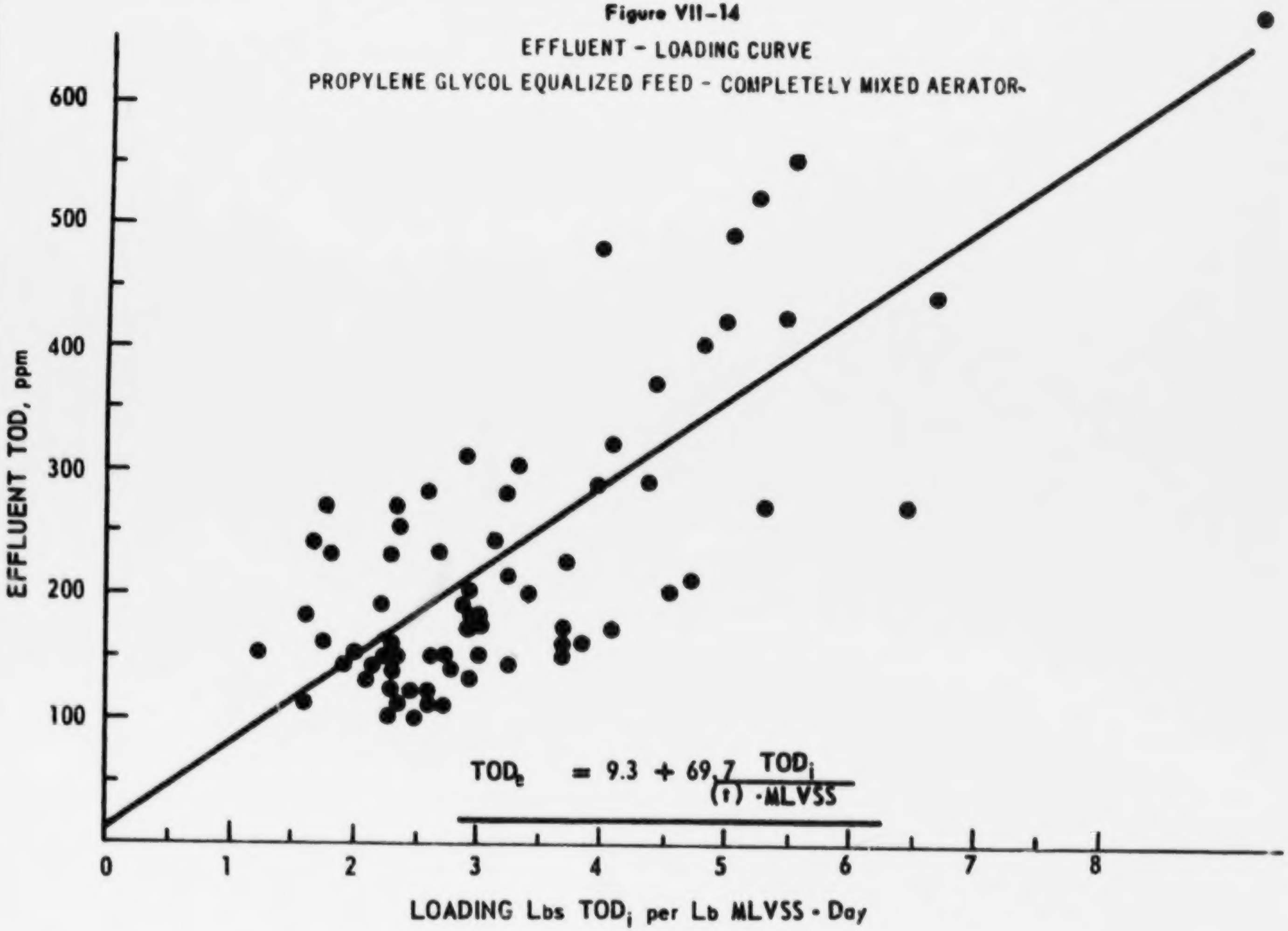
The stirrer, at 60 rpm, was just enough to keep the suspended solids mixed when the air was cut off. The temperature of the aerator was controlled by immersing it in a water bath.

The unit was fed with the same pretreated waste at the same loading and recycle as in the pilot plant, then equilibrated over a period of 20 hours. At this time, the air was shut

Figure VII-14

EFFLUENT - LOADING CURVE

PROPYLENE GLYCOL EQUALIZED FEED - COMPLETELY MIXED AERATOR.



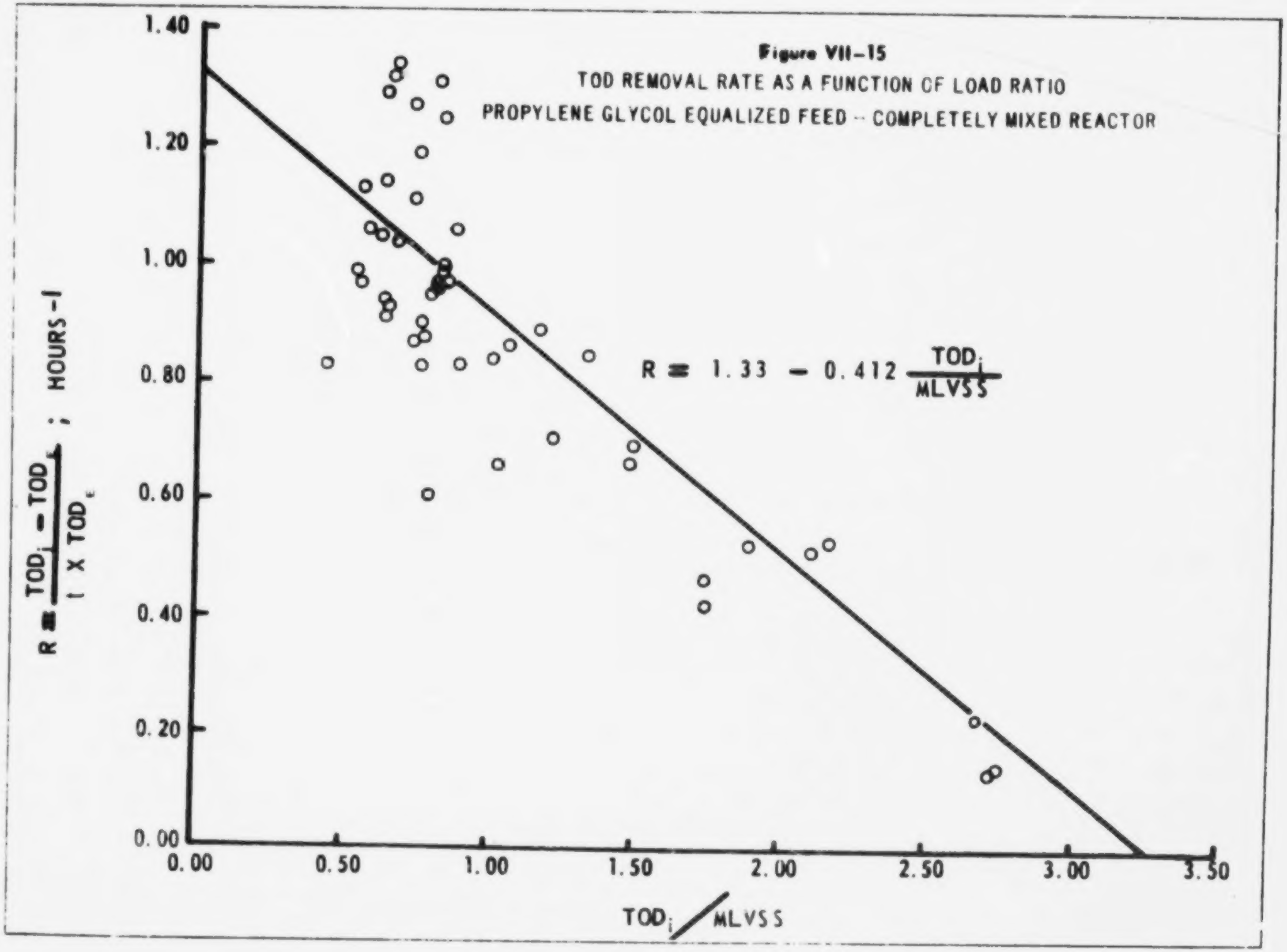


Figure VII-15

TOD REMOVAL RATE AS A FUNCTION OF LOAD RATIO

PROPYLENE GLYCOL EQUALIZED FEED -- COMPLETELY MIXED REACTOR

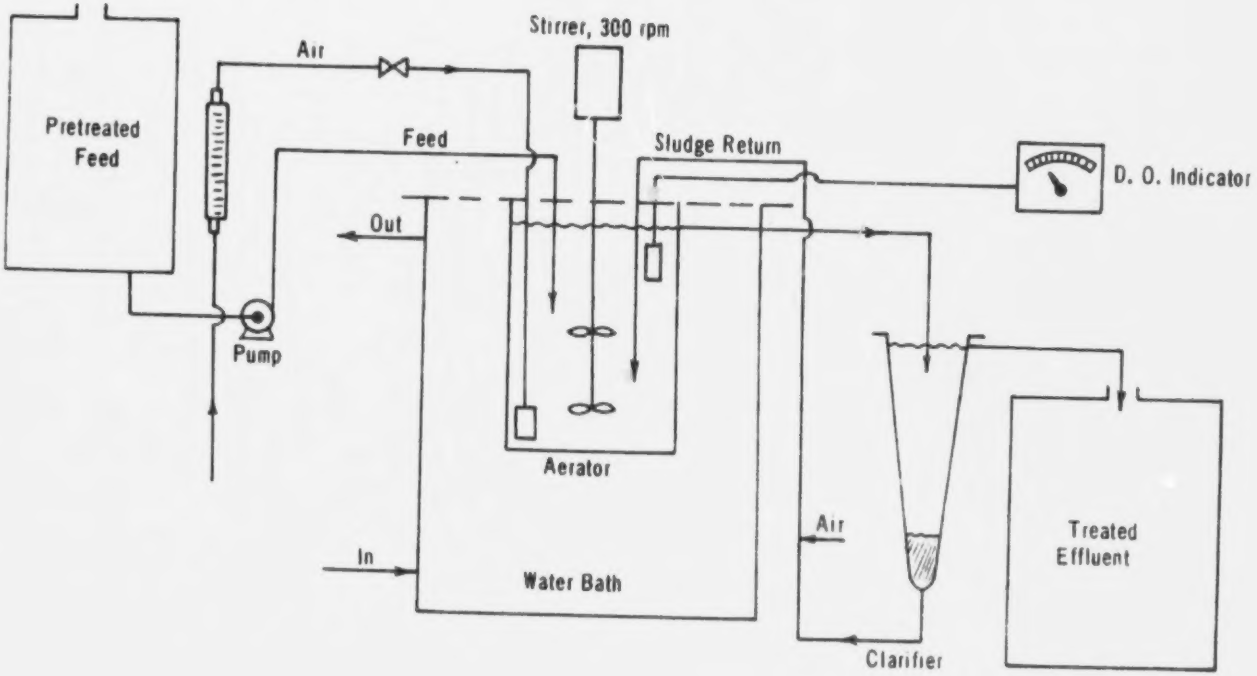


Figure VII-16
CONTINUOUS LABORATORY UNIT FOR
OXYGEN UPTAKE MEASUREMENTS

Pretreated Feed
Air
Feed
Stirrer, 300 rpm
Sludge Return
D. O. Indicator
Out
Pump
Aerator
In
Water Bath
Air
Clarifier
Treated Effluent

off and the dissolved oxygen concentration measured as a function of time. The air was then turned back on for 5 minutes, but without any feed or sludge return. The air was then cut off, and the oxygen uptake recorded under no-loading conditions.

A typical oxygen uptake measurement is shown in Figure VII-17. The slope of the oxygen depletion line with respect to time was found to be the same whether or not a nitrogen blanket was used on the surface of the aerator. The surface re-adsorption of oxygen at the mixed liquor interface is negligible during the first few minutes of the test at the mixing speed of 60 rpm and the operating level of around 3 ppm. oxygen.

The oxygen uptake was measured at various loading levels. The oxygen demand (pounds per pound MLVSS per day) is shown as a function of removal in Figure VII-18. The slope of the line of best fit represents the oxygen consumed per pound of TOD removed (a = 0.256). The intercept b = 0.13 is the oxygen demand of the endogenous respiration of the bacteria. This value checks the measured value very closely. From Figure VII-17, the rate of oxygen uptake under no loading is seen to be 0.19 ppm. per minute when the MLVSS averaged 1970 ppm. over a 24-hour period. This corresponds to b = 0.139 in pounds O.C. per pound MLVSS per day.

The ratio of a/b in this high salt system is about 2. For fresh water activated sludge the value of a/b is more likely to be 5 or 6. This lower ratio of the active oxygen demand to the endogenous respiration seems to be a characteristic of the halophilic bacteria, that differentiates it from fresh water bacteria.

The effect of temperature on the oxygen uptake rate is shown in Figure VII-13. The relationship can be represented by:

$$K_T = K_{20°} \cdot 1.042^{(t-20)}$$

where

K_T = Oxygen uptake rate coefficient at t°C.
$K_{20°}$ = Oxygen uptake rate coefficient at 20°C.
t = Temperature in °C.

The energy of activation ΔE as calculated from these temperature data, is 7250 Cal./mol. which is about half of the value reported for fresh water activated sludge (Eckenfelder, 1961).

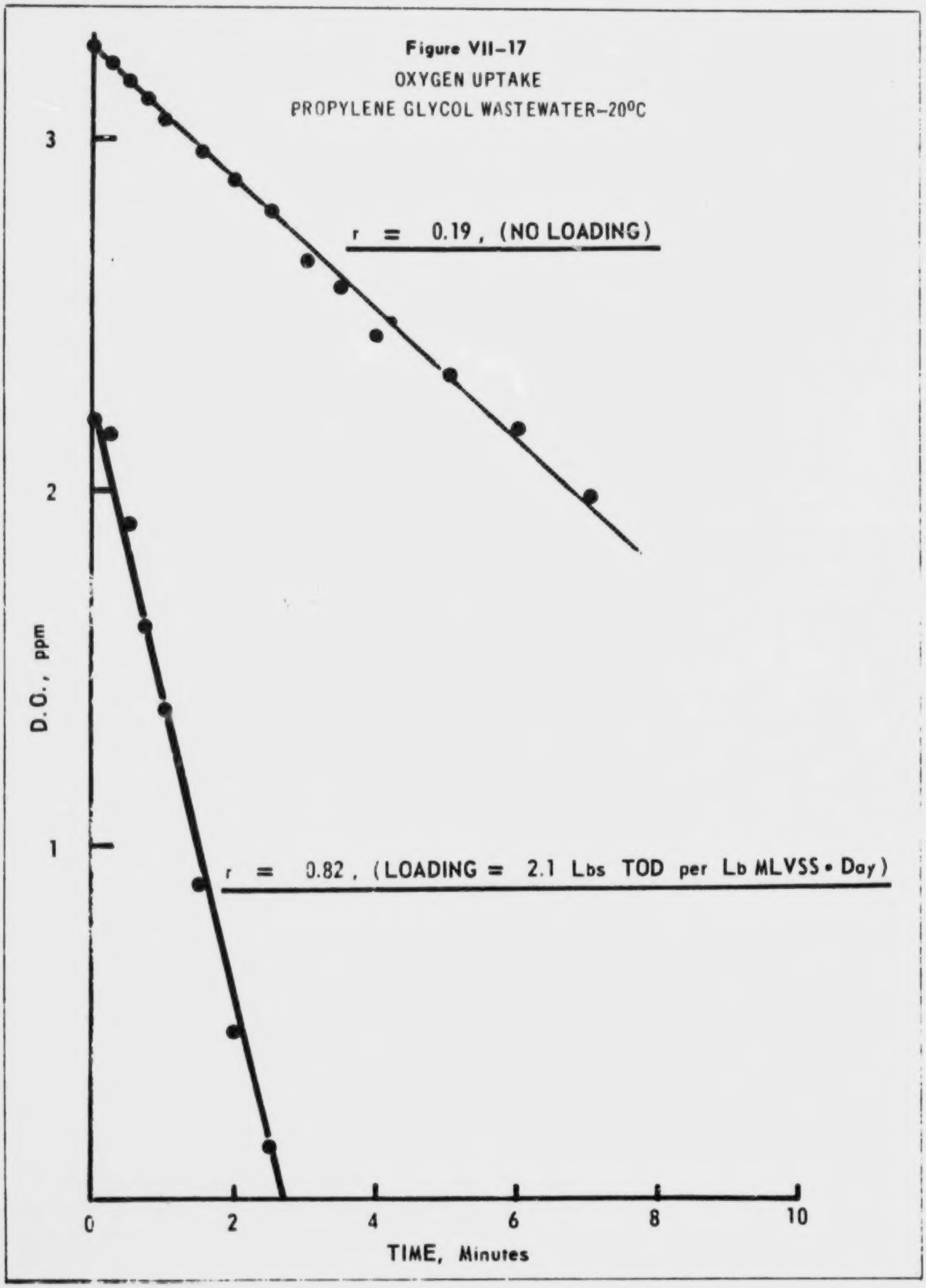
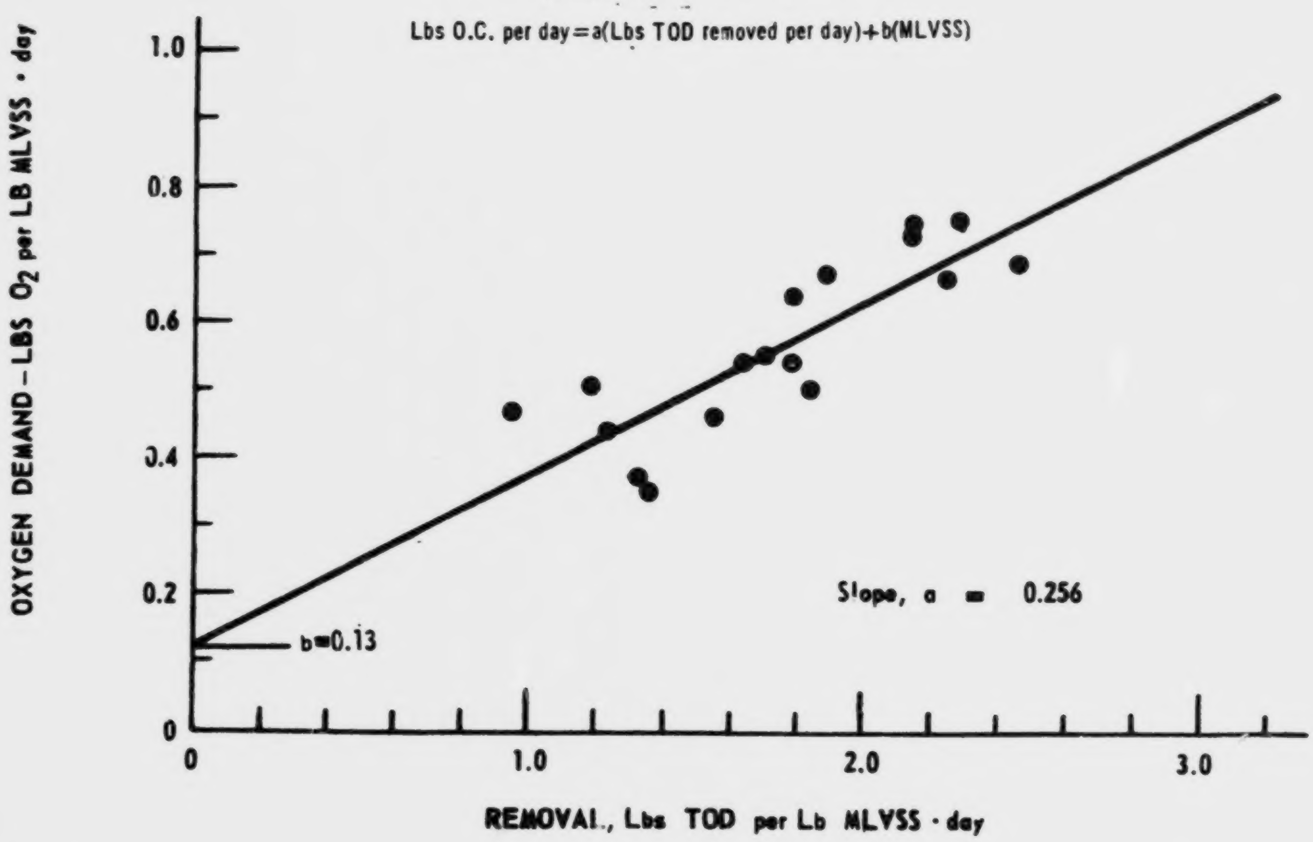


Figure VII-17
OXYGEN UPTAKE
PROPYLENE GLYCOL WASTEWATER–20°C

Figure VII-18
OXYGEN UTILIZATION
(Temperature 20° to 25°C)



Oxygen Mass Transfer Rate

The oxygen saturation level in the saline wastewater is only 0.42 to 0.46 that of tap water, principally because of the high salt content of the waste. In an activated sludge system the oxygen transfer rate is given by:

$$dc/dt = K_{La}[C_s - C] - r$$

where

C_s = oxygen saturation in the wastewater

c = equilibrium or operating oxygen concentration

r = oxygen uptake rate.

At steady state dc/dt = o, therefore:

$$K_{La} = \frac{r}{(C_s - C)}$$

In the non-steady state method used to determine K_{La}, the oxygen in the water sample was depleted, then the sample re-aerated and the dissolved oxygen increased with time recorded. By plotting the oxygen deficit $(C_s - C)$ versus time on a semi-log paper, a straight line is obtained with a slope equal to K_{La}, therefore:

$$K_{La} = \frac{\Delta \ln (Cs - C)}{\Delta t}$$

The laboratory activated sludge unit was used to measure the oxygen mass transfer coefficients K_{La} for tap water and the mixed liquor. The ratio of K_{La} in the waste to K_{La} in tap water (α) was found to be very difficult to determine, since K_{La} depends on the nature of the wastewater (surface activity), the degree of surface renewal ($K_{La} = K_L \frac{A}{V}$), and the degree of turbulence or the mechanics of aeration.

In the laboratory equipment under quiescent conditions, with air transfer through the surface of the liquid and the mixer at very low speed, an α value less than 0.5 for the wastewater feed was obtained. This is due to the high concentration of surface active organics in the wastewater feed, the presents a barrier for oxygen transfer at the surface. When K_{La} was determined for the treated wastewater using a submerged diffuser, and applying the steady state method, the values of α were found to be unreasonably high (over 2.0).

The effect of the turbulence created by aeration on the oxygen transfer rate is shown in Figure VII-19. The higher rate of surface renewal (A/V) in the wastewater as compared to tap water, was indicated by a noticable reduction in bubble size, and is the reason for the determined α values over 1.0. The determinations of K_La in tap water and the treated waste at an aeration rate of 600 c.c./min. are plotted in Figure VII-20. For aeration rates of 400 to 900 c.c./min. in the 4.1 liter vessel, the α value remained constant at around 1.2.

Sludge Production Rate

The sludge production over a 24-hour period was measured in both the laboratory equipment and in the pilot plant during steady state operation on an equalized feed. Initially the wasting of settled sludge or mixed liquor was batchwise, but a pump was then installed to continuously waste a measured amount of mixed liquor in order to maintain the mixed liquor volatile suspended solids (MLVSS) in the aeration tank at an almost constant value over a 24-hour period. The volatile suspended solids (VSS) formed each day was calculated by using the following equation:

$$\text{Lbs. VSS formed/lb. MLVSS}\cdot\text{day} = \frac{V_W C_W + (C_F - C_O)V_A + V_E C_E}{V_A C_{avg.}}$$

where

V_W = wasted volume of mixed liquor

V_A = volume of aeration tank

V_E = volume of effluent

C_O = initial MLVSS in aeration tank

C_F = final MLVSS in aeration tank

C_W = MLVSS in wasted mixed liquor

C_E = VSS in treated effluent

$C_{avg.}$ = $(C_O + C_F)/2$

The laboratory results and the batch wasting from the pilot plant are shown in the lower line of Figure VII-21. The intercept of -0.065 checks well with the measured loss of solids, when the sludge is aerated, of 6% per day under endogenous conditions.

The continuous wasting data plotted in the upper line of Figure VII-21 has a slope of 0.133 and an intercept of -0.0205. It is believed that the continuous wasting data are more accurate.

Figure VII-19

EFFECT OF AERATION RATE ON OXYGEN TRANSFER

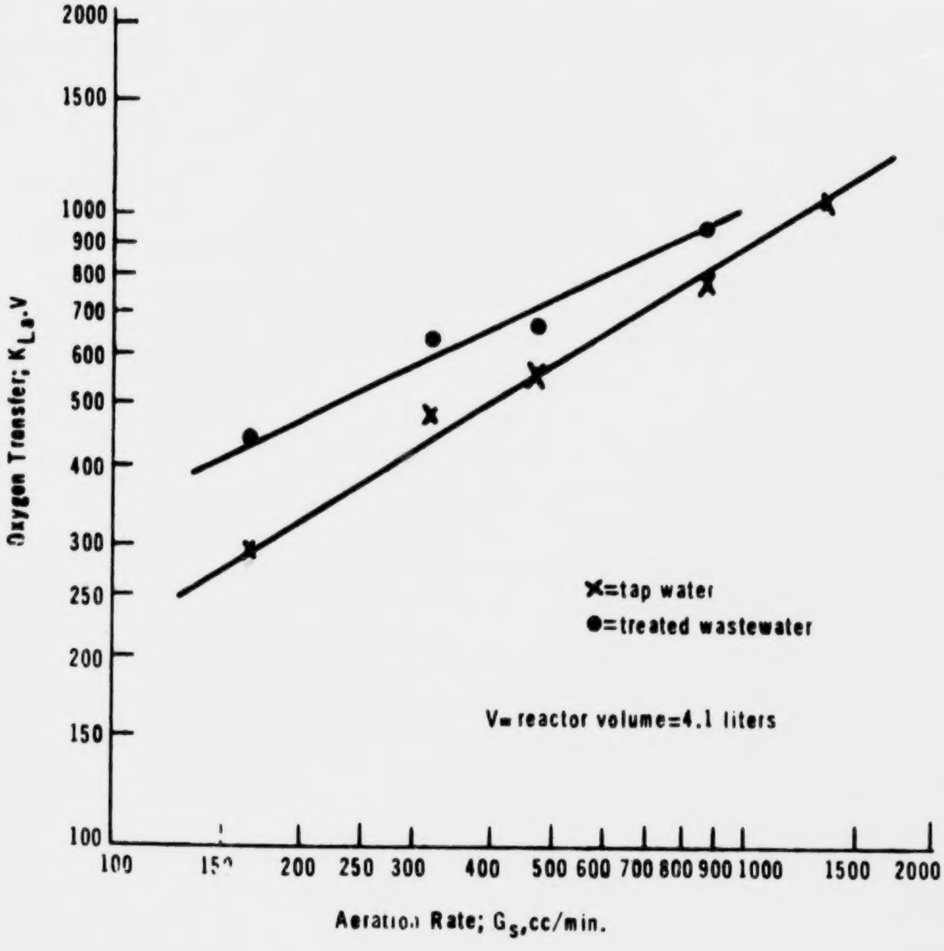


Figure VII-20

OXYGEN MASS TRANSFER

The non-steady state method)

Temperature 20°C

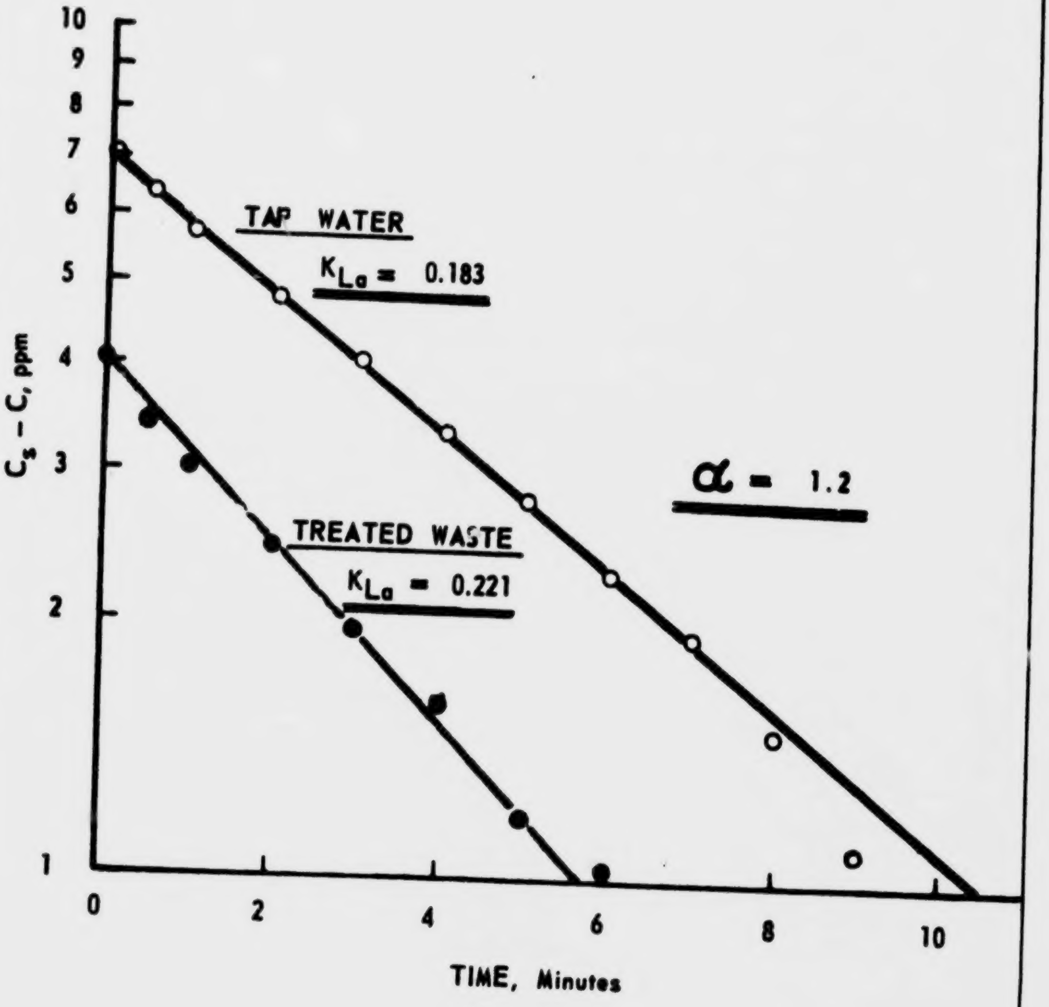
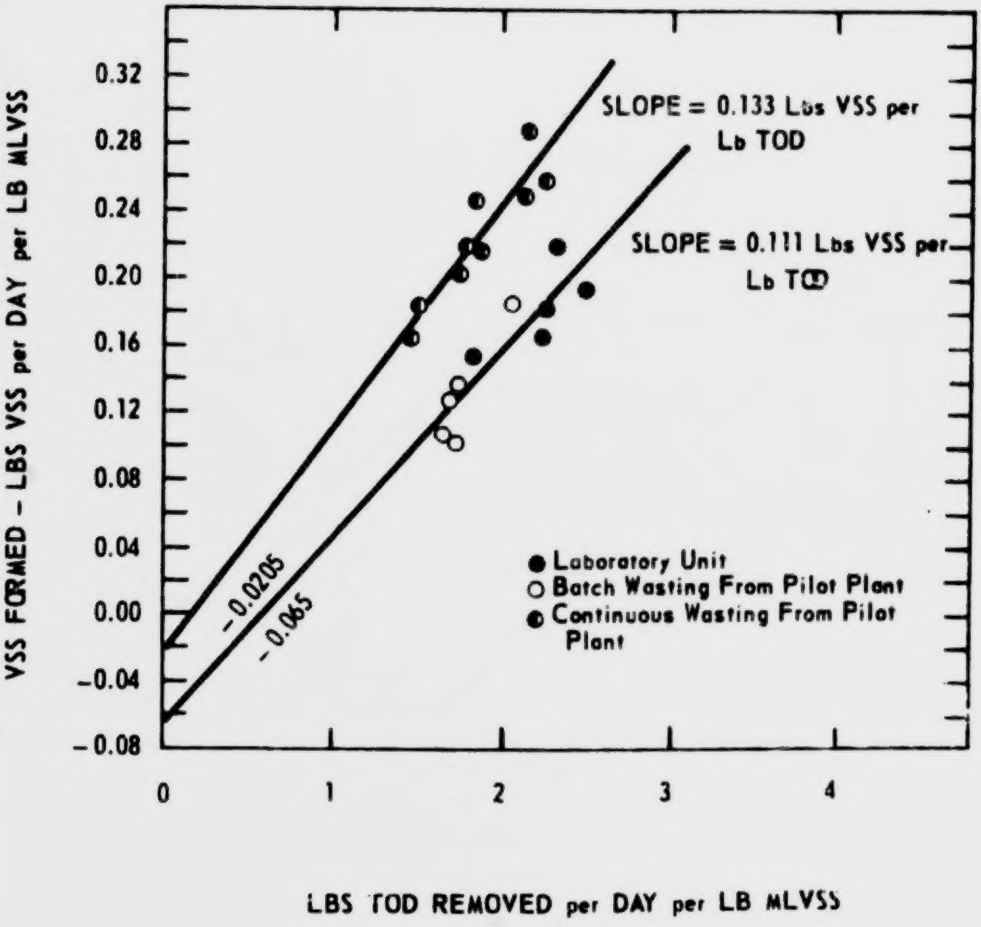


Figure VII-21

GROSS SOLIDS FORMATION

LBS VSS FORMED per DAY = C(Lbs TOD Removed per Day) + d(MLVSS)



Liquid-Solid Separation

The sludge formed during most of the pilot plant operation was found to have a very low volume index with very good settling properties.

Air flotation was tried as a method of sludge separation from the mixed liquor. The sludge particles were broken down to a very fine suspension that was difficult to handle, since only part of it floated to the surface. The addition of organic flocculants to the air flotation unit did not improve the separation.

The sludge settling properties were determined in a 6 foot deep test cylinder with sampling points at 2, 4, 5 and 6 foot depths. Sludge samples from the aeration tank of the pilot plant were well mixed and the original suspended solids (C_o) measured. Samples were drawn off at selected time intervals at 2, 4 and 5 foot depths. The concentration of suspended solids was measured at each sampling point and each time. The amount removed from the initial concentration (C_o) was plotted against the respective depths and times. Curves are then approximated by connecting points of equal concentrations. These resultant settling path curves for the sludge of different original concentrations are shown in Figures VII-22, VII-23 and VII-24.

The sludge volume index shown on each figure was determined using the standard method. The final sludge concentration from the 6 foot tap at the end of each test averaged about 32,000 ppm. for all sludges tested.

With an initial bacterial concentration of over 1100 ppm., 90% suspended solids removal was obtained in about 20 minutes. Sludges with concentrations less than 1000 ppm. took much longer to settle.

During periods of disturbances in the plant operation, samples of the sludge had a sludge volume index (SVI) as high as 100, for which a removal of 70% required over 100 minutes. Under normal operating conditions, the sludge volume index varied between 50 and 60, and 90% of the sludge settled in less than 20 minutes. These data can be used, with appropriate scale-up factors, for the design of settling vessels for the sludges produced in any size activated sludge plant.

The overflow from the settling tank after the activated sludge treatment is usually slightly turbid, with a TOD of 200 to 300 ppm., although it contains no residual organics that are present in the feed. Several flocculants were tested for clarification of the treated wastewater. Among

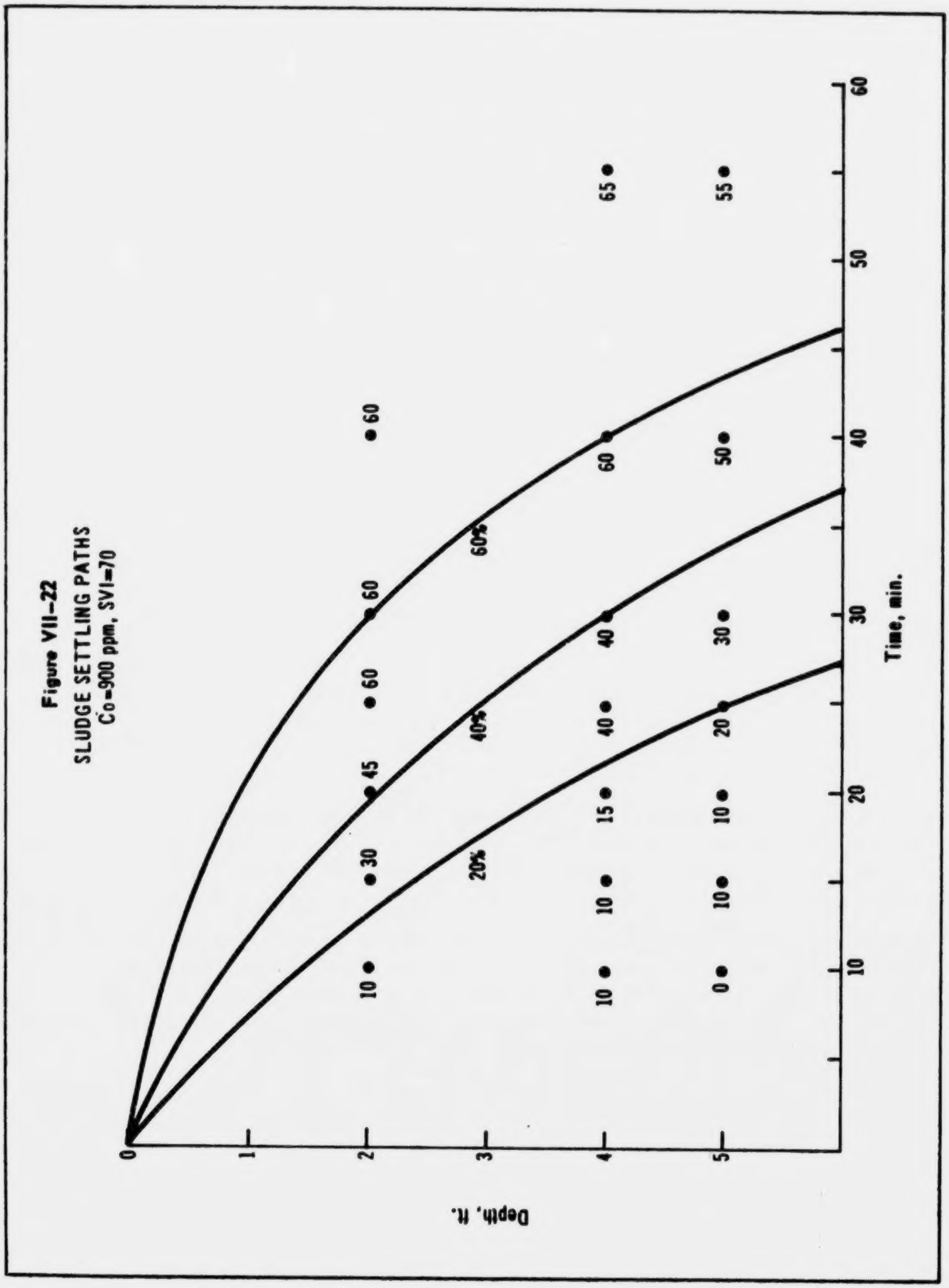


Figure VII-22
SLUDGE SETTLING PATHS
Co=900 ppm, SVI=70

Figure VII-23

SLUDGE SETTLING PATHS

Co=1100 ppm, SVI=53

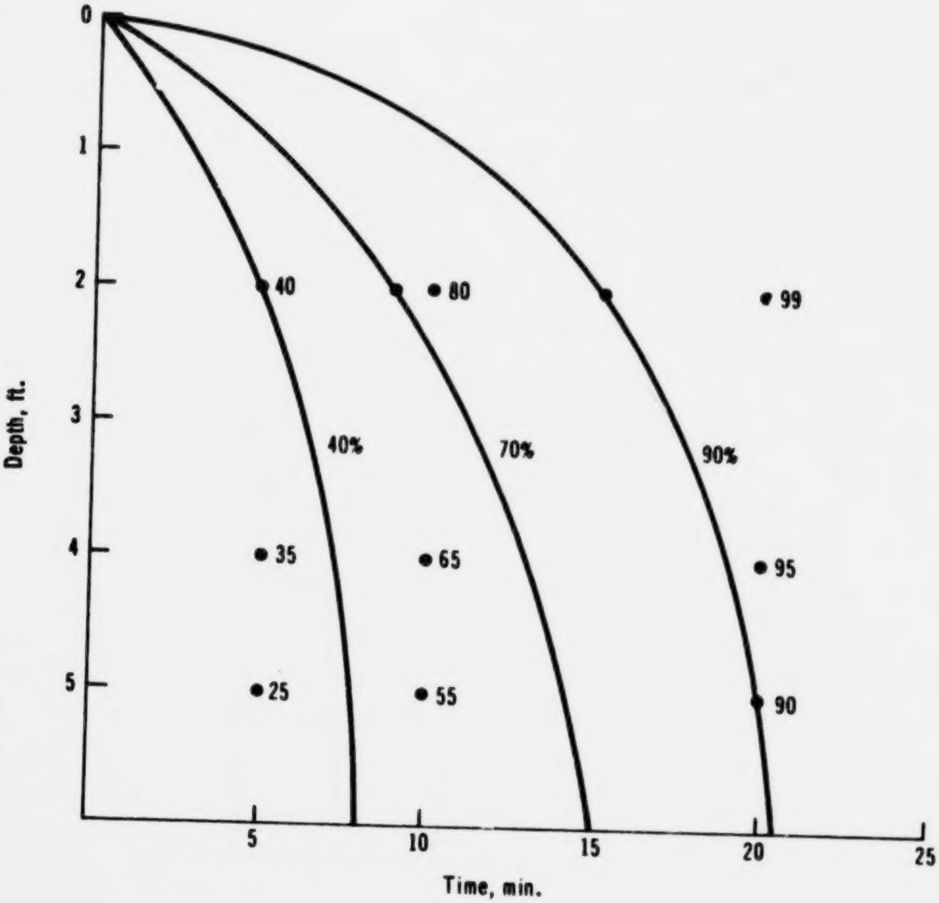
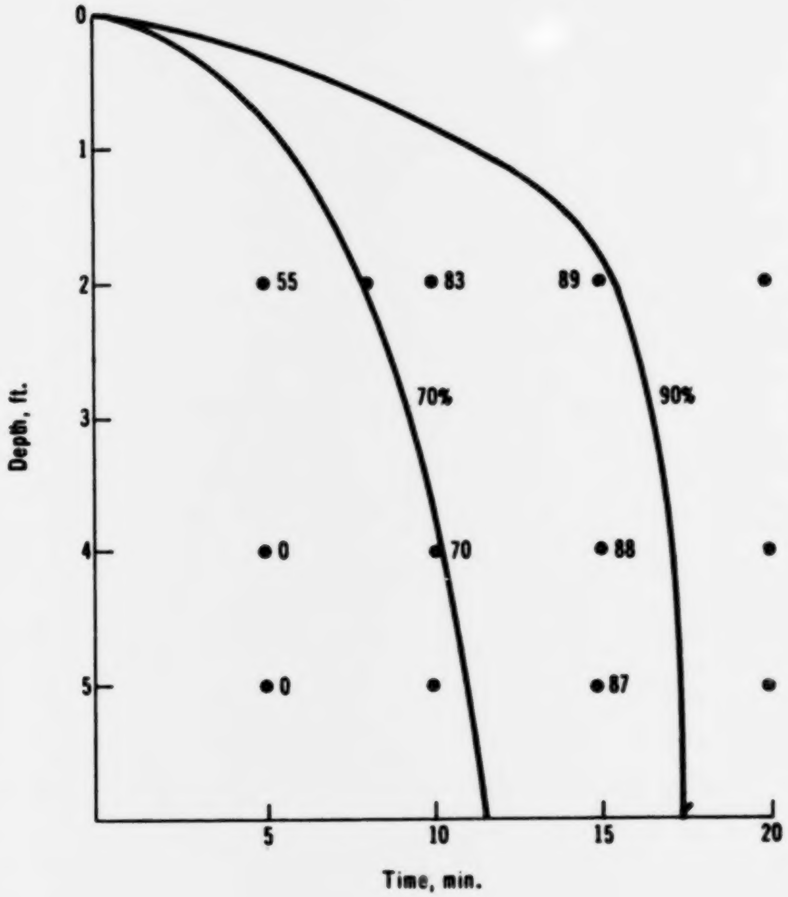


Figure VII-24

SLUDGE SETTLING PATHS

Co=1700 ppm, SVI=42



those tested were Puriflocs® (cationic, anionic and nonionic), alum and ferric salts. The best system examined required 150 to 200 ppm. alum at a pH of 7.5 to 8.0 (adjusted with sodium hydroxide). The TOD of the clarified effluent is usually reduced by 50% after clarification.

The flocculation step is not felt to be necessary, except when the treated wastewater is to be reused in other plant operations, such as a feed to chlorine cells, where the remaining TOD is objectionable.

Carbon and Oxygen Balance

A material balance around the organic carbon and oxygen consumed was calculated for 18 days of steady state operation of the pilot plant. Sample calculations are given in Table VII-2, for 4 days of operation, showing the ranges of parameters calculated.

The weight of carbon in the volatile suspended solids (VSS) formed was calculated as 0.53 of the weight, the ratio of carbon to the total weight in the bacterial cell formula ($C_5H_7NO_2$).

The weight of oxygen consumed for synthesis of the cells was also calculated as 32/113 of the weight of VSS formed. The carbon oxidized to CO_2 was calculated by difference. The total organic carbon of the homogenized mixed liquor sample was found experimentally to be about 50% of the VSS of the samples, which increased the confidence in using $C_5H_7NO_2$ as the formula for the bacterial cells.

Optimization of Nutrient Requirements

At the start of the pilot plant operation, the nutrient solution was added at a rate that would produce 100 ppm. nitrogen and 20 ppm. phosphorus in the feed to the aeration tank. Ammonia nitrogen, total nitrogen and phosphate were analyzed in the feed and the treated effluent over a period of two months and the feed rate adjusted accordingly. As a result, the rate of nutrient addition, for the range of TOD values up to 2000 ppm., has been reduced to 50-60 ppm. N and 10-12 ppm. P, with the treated effluent containing 20-30 ppm. ammonia N and 1-3 ppm. P.

The halophilic bacterial culture requires higher concentrations of nitrogen and lower concentrations of phosphorus than do the fresh water cultures reported in the literature. A ratio of TOD:N:P of 300:10:1 was found to be the optimized value for the nutrient requirement. For an average of 1500 ppm. TOD in the propylene glycol wastewater (BOD_5 = 540), 50 ppm., ammonia

TABLE VII-2

CARBON AND OXYGEN BALANCE OF THE ACTIVATED SLUDGE PROCESS

	Days of Operation			
	1	2	3	4
Feed, GPD. (A)	650	650	650	650
Effluent, GPD. (B)	625.2	600	599.7	602
TOD removed, ppm. (C)	1155	1470	1115	1060
MLVSS, ppm. (D)	1712	1660	1628	1312
TOC In, ppm. (E)	257	266	255	265
TOC Out, ppm. (F)	38	23	31	37
Lbs. VSS formed per lb. TOD removed (H)	0.116	0.089	0.136	0.230
Lbs. TOD removed ($K = 8.85\ AC$)	6.64	8.47	6.42	6.1
Lbs. VSS formed ($L = HK$)	0.77	0.755	0.874	1.4
Lbs. Carbon In ($M = 8.85\ AE \times 10^{-6}$)	1.48	1.53	1.47	1.53
Lbs. Carbon Out ($N = 8.85\ BF \times 10^{-6} + 0.53\ L$)	0.618	0.524	0.627	0.939
% Carbon to CO_2 ($\frac{M-N}{M} \times 100$)	58	65	57	39
Oxygen Consumed, O.C. $[(M-N)\frac{32}{12} + (L)\frac{32}{113}]$	2.52	2.87	2.49	2.05
Lbs. O.C./lb. TOD removed ($\frac{O.C.}{K}$)	0.380	0.338	0.386	0.337

Average of 18 days of operation:

Lbs. VSS formed/lb. TOD removed = 0.133
% Carbon oxidized to CO_2 = 58%
Lbs. O.C./lb. TOD removed = 0.4

N, and 5 ppm. phosphate P fed gave a residual of 8 ppm. N and 1-2 ppm. P in the effluent.

Summary of Design Parameters

The activated sludge pilot plant was operated both as a plug flow and as a completely mixed reactor. Results show that an advantage exists for the completely mixed mode of operation especially if the feed is equalized to dampen the changes in organic loading. Removal efficiencies of over 90% were obtained over a long operational period when the system was completely mixed, and at retention time of less than 9.0 hours. The average removal efficiencies of the plug flow operation were about 84% for a retention time of 12 hours. The results of the plug flow operation checks the laboratory batch results, while the completely mixed mode of operation resulted in higher removal efficiencies at lower residence times and higher organic loading than can be tolerated in the plug flow reactor. The measured and calculated design parameters are summarized in Table VII-3.

E. Polishing of the Biotreatment Plant Effluent With Activated Carbon

The effluent from the activated sludge treatment does not contain any of the organic components that were originally dissolved in the feed wastewater. The effluent, however, still contains dissolved organics (the degradation products of the bacterial cells) in concentrations varying from 25 to 50 mg/l total organic carbon (TOC) or 80 to 150 mg/l of total oxygen demand (TOD).

Polishing of the biotreatment plant effluent with activated carbon to produce a sodium chloride solution suitable for reuse as feed to the chlorine cells was studied in the laboratory. An activated carbon, Witco, grade 517, 20-40 mesh, was used in a packed column for the polishing of the effluent. Several hundred gallons of the polished effluent were produced containing less than 10 mg/l of total organic carbon.

The capacity of the activated carbon for the dissolved organics averaged about 1.5 pounds per 100 pounds of carbon. Regeneration with steam at 300°F failed to reactivate the carbon. Thermal regeneration in a muffle furnace is probably required.

The polished effluent was saturated with salt, treated with soda-ash to remove any traces of calcium, and then fed to two laboratory cells for a period of 10 days. The cell conditions and gas analysis were recorded. No change was noted

TABLE VII-3

SUMMARY
GLYCOL WASTE TREATMENT
ACTIVATED SLUDGE DESIGN PARAMETERS

Removal efficiency:	92%
Optimum temperature:	30-35°C.
Allowable temperature range:	17-40°C.
Nutrient requirements:	TOD:N:P = 300:10:1
Removal rate:	1 - $TOD_e = 9.3 + 69.7 \left(\frac{TOD_i}{t \times MLVSS}\right)$ 2 - $R = \frac{TOD_i - TOD_e}{t \times TOD_e} = 1.330-0.42 \left(\frac{TOD_i}{MLVSS}\right)$
Oxygen utilization:	lbs. O.C./day = 0.256 (lbs. TOD removed/day) + 0.13 (lbs. MLVSS), at 20°C.
Oxygen transfer:	$\beta = 0.47$ $\alpha = 1.2$
Sludge production:	lbs. VSS formed/day = 0.133 (lbs. TOD removed/day) - 0.021 (lbs. MLVSS)

TOD_e = total oxygen demand in effluent.

TOD_i = total oxygen demand in feed plus recycle.

O.C. = oxygen consumed.

VSS = volatile suspended solids

β = ratio of oxygen saturation in the mixed liquor to that in tap water.

α = ratio of oxygen transfer rate in the mixed liquor to that in tap water.

in any of the cell operating characteristics. The usual Orsat analysis of the chlorine showed no increase in CO_2. The organic impurities in the feed brine and in the cell effluent were so low that their presence is not expected to cause any long-term problems.

The very low capacity of the activated carbon for the dissolved organic residues in the effluent from the biotreatment plant, and the need for thermal regeneration of the carbon rather than an in-situ regeneration with steam, appears to make the polishing step too expensive to serve as a reuse process.

Large scale operation of the activated sludge process at an optimum recycle ratio combined with proper flocculation of the residual turbidity of the effluent may produce an effluent quality sufficient for reuse as a feed to chlorine cells without the need for polishing with activated carbon.

SECTION VIII

CONCEPTUAL DESIGN OF A 6 MGD ACTIVATED SLUDGE WASTE TREATEMENT PLANT

Based on the results of the successful operation of the pilot plant for the bio-oxidation of the organics in the glycol wastewater, a conceptual design of a 6 MGD activated sludge waste treatment plant has been prepared and the capital requirements and operating cost estimated.

A typical chemical plant producing propylene glycol, by the chlorohydrin process, at a rate of about 1.2 million pounds per day would also produce a wastewater stream of 6 million gallons per day. This wastewater, resulting from the hydrolysis of the chlorohydrin to the oxide, is a brine containing dissolved organic components with a pH of 11 to 12 and a temperature of about 190°F. as it leaves the production plant. The cost estimates and economic evaluation of the process is based on prices prevailing on the Gulf Coast during the period 1970-1971.

A. Process Description and Plant Design

The design of the activated sludge plant is based on a feed of the composition and flow rate as shown in Table VIII-1. A flow diagram (Figure VIII-1) and a general plant layout (Figure VIII-2) show the sequence of operations and the relative positions of the equipment, respectively. The major equipment and instrumentation is listed in Tables VIII-2 and VIII-3. Details and design calculations are included in Appendix D to this report.

Neutralization

The pH of the feed is reduced to about 9.5 by the addition of hydrochloric acid or sulfuric acid, whichever is most economically available at the plant site. The acid requirement, equivalent to 90% of the excess caustic in the feed, is calculated as 14.5 gpm. of 38% HCl or 5 gpm. of 98% H_2SO_4. The acid (38% HCl) is pumped from a 30,000 gallon surge tank into the feed line before the equalization and cooling pond, where the pH is controlled at about 9.5 (Figure VIII-3). It is expected that during the 2-day retention of the feed in the cooling pond, the reaction with carbon dioxide from the atmosphere, will reduce the pH to between 8.0 and 8.5.

Cooling and Equalization

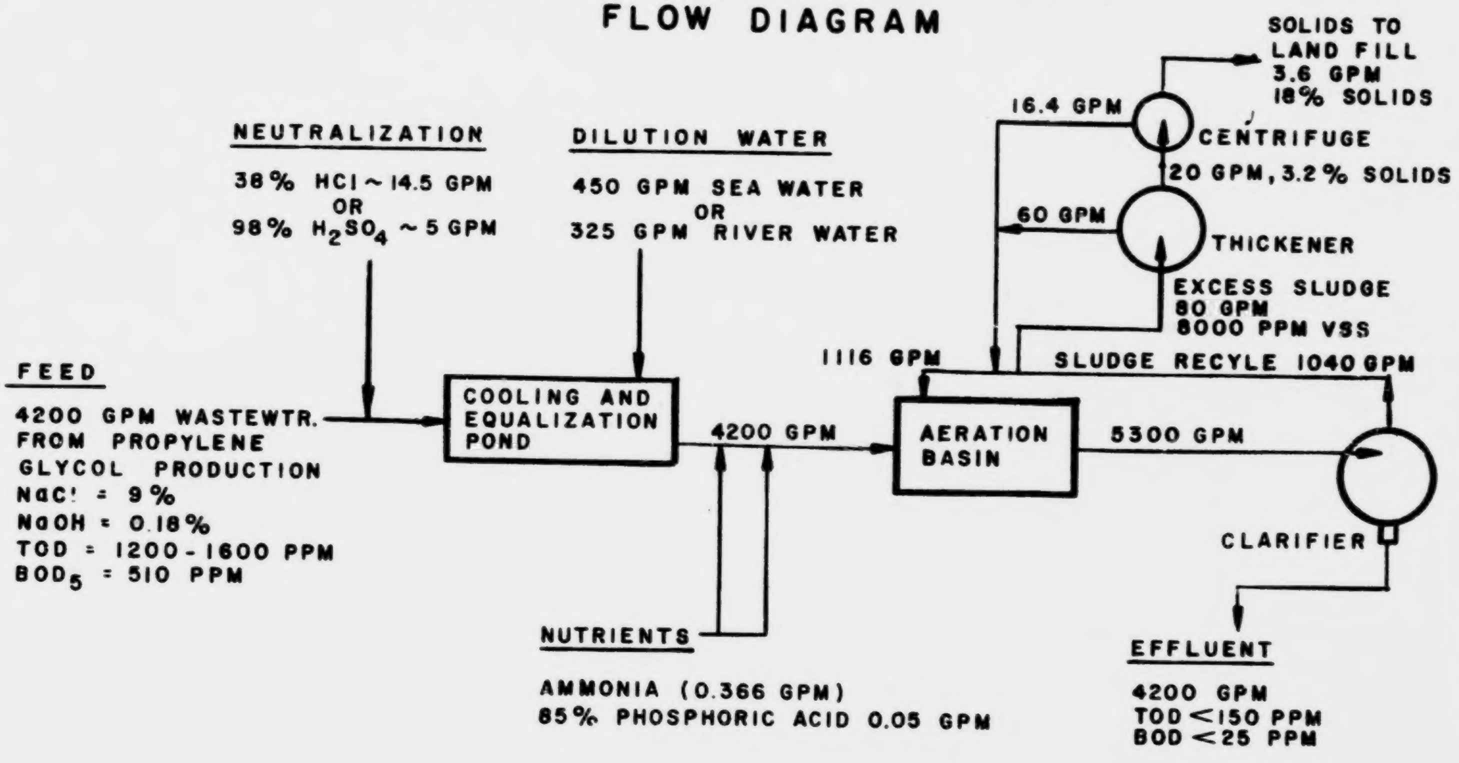
The cooling of the feed from a temperature of 180°F. to 105°F. during the summer months, when the air maximum daily

TABLE VIII-1

DESIGN FEED
6 MGD ACTIVATED SLUDGE WASTEWATER TREATMENT PLANT

Flow Rate	4200 GPM (53.2×10^6 lbs./day)
NaCl	9.0%
Sp. Gr./20°C	1.063
NaOH	0.18%
Temperature	180°F.
TOD	1400 ppm.
BOD_5	510 ppm.
Propylene Glycol	640 ppm.

FIGURE VIII-1
ACTIVATED SLUDGE PLANT - 6 MGD
FLOW DIAGRAM



FEED
4200 GPM WASTEWTR.
FROM PROPYLENE
GLYCOL PRODUCTION
NaCl = 9%
NaOH = 0.18%
TOD = 1200-1600 PPM
BOD5 = 510 PPM
NEUTRALIZATION
38% HCl ~ 14.5 GPM
OR
98% H2SO4 ~ 5 GPM
DILUTION WATER
450 GPM SEA WATER
OR
325 GPM RIVER WATER
COOLING AND EQUALIZATION POND
4200 GPM
NUTRIENTS
AMMONIA (0.366 GPM)
85% PHOSPHORIC ACID 0.05 GPM
1116 GPM
AERATION BASIN
5300 GPM
SLUDGE RECYLE 1040 GPM
16.4 GPM
60 GPM
SOLIDS TO
LAND FILL
3.6 GPM
18% SOLIDS
CENTRIFUGE
20 GPM, 3.2% SOLIDS
THICKENER
EXCESS SLUDGE
80 GPM
8000 PPM VSS
CLARIFIER
EFFLUENT
4200 GPM
TOD <150 PPM
BOD <25 PPM

FIGURE VIII -2
ACTIVATED SLUDGE PLANT - 6 MGD
PLANT LAYOUT

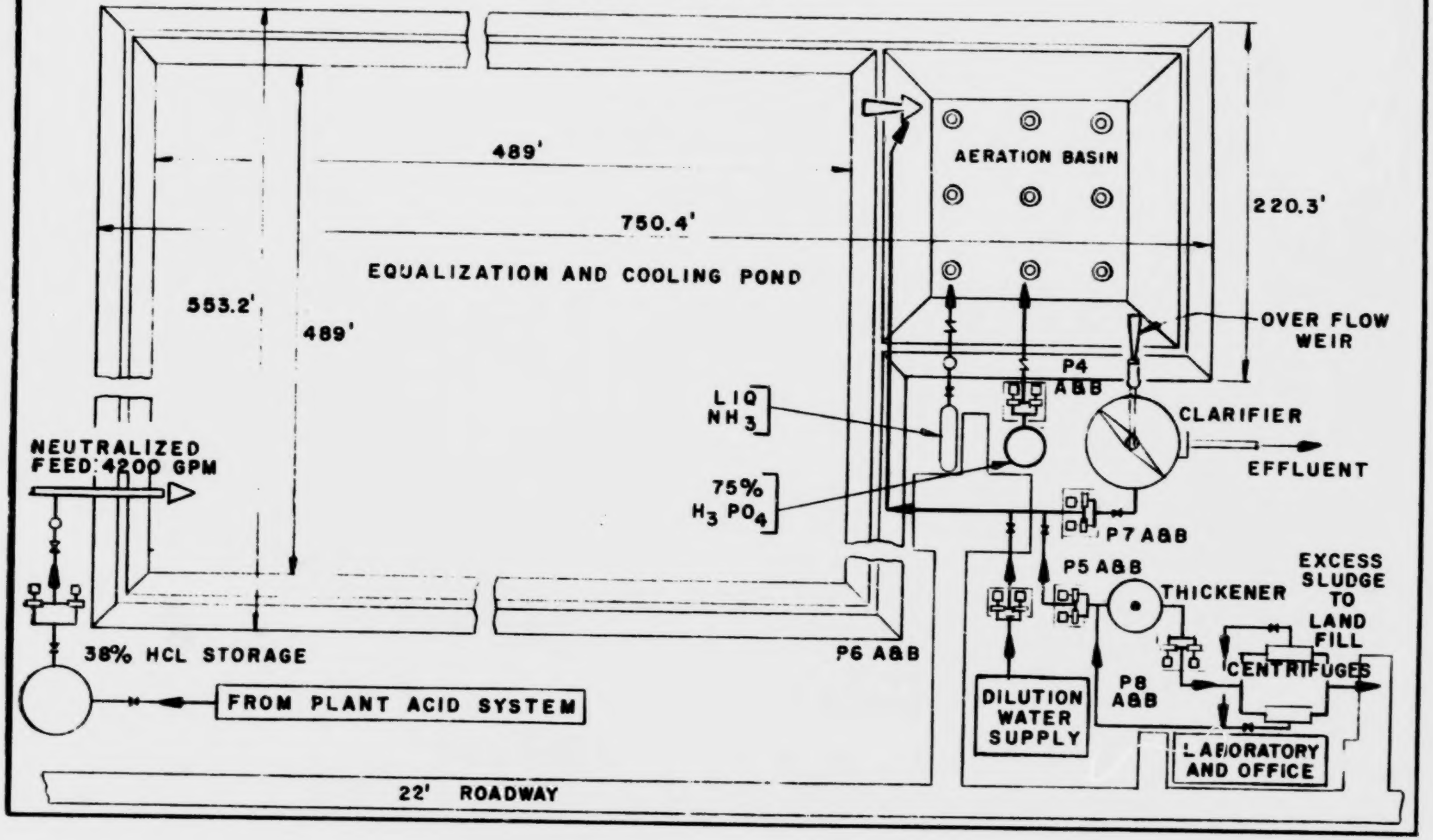

489'
750.4'
EQUALIZATION AND COOLING POND
553.2'
489'
AERATION BASIN
220.3'
OVER FLOW WEIR
P4 A&B
LIQ NH3
75% H3 PO4
CLARIFIER
EFFLUENT
NEUTRALIZED FEED 4200 GPM
P7 A&B
P5 A&B
THICKENER
EXCESS SLUDGE TO LAND FILL
CENTRIFUGES
38% HCL STORAGE
P6 A&B
FROM PLANT ACID SYSTEM
DILUTION WATER SUPPLY
P8 A&B
LABORATORY AND OFFICE
22' ROADWAY

TABLE VIII-2

MAJOR EQUIPMENT
6 MGD ACTIVATED SLUDGE WASTEWATER TREATMENT PLANT

D-1	38% HCl Surge Tank
EC-1	Equalization and Cooling Ponds
D-2	Ammonia Storage Tank
D-4	Phosphoric Acid Storage Tank
A-6	Aeration Basin
Cl-7	Clarifier
THK-8	Sludge Thickener
CF-9A CF-9B	Centrifuges
P-1A P-1B	38% HCl Acid Pumps
P-4A P-4B	Phosphoric Acid Supply Pumps
P-6A P-6B	Dilution Water Pumps
P-7A P-7B	Sludge Recycle Pumps

Table VIII-2 (Continued)

P-8A	Sludge Pumps
P-8B	
P-9A	Effluent Return Pumps
P-9B	

TABLE VIII-3

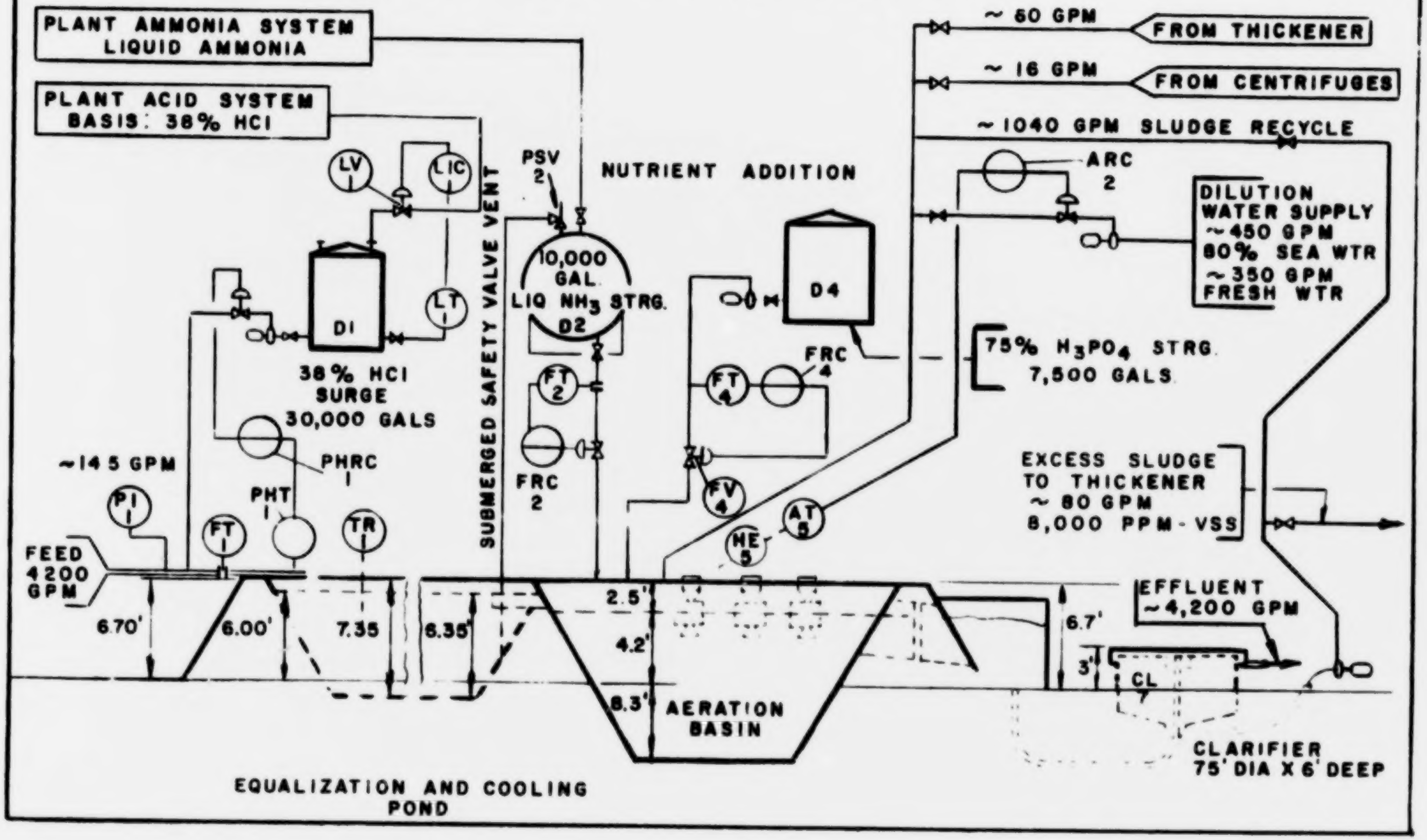
MAJOR INSTRUMENTATION
6 MGD ACTIVATED SLUDGE WASTEWATER TREATMENT PLANT

LT-1	Level Control, HCl Surge Tank
L1C-1	
LV-1	
LI-1	
pHT-1	pH Measurement, Acid Flow Rate Control
pHRC-1	
pHV-1	
FO-1	Feed Flow Rate Measurement
FE-1	
FT-1	
FR-1	
LT-2	Level Control, Ammonia Storage Tank
L1C-2	
LV-2	
FO-2	Ammonia Flow Control
FRC-2	
FT-2	
FV-2	
LT-4	Level Control Phosphoric Acid Storage
LI-4	
FT-4	

Table VIII-3 (Continued)

FO-4 FRC-4 FV-4	Flow Control, Phosphoric Acid
AT-5 ARC-5 AV-5	Dilution Flow Control, Density Measurement
FT-5 FE-5 FE-6	Parshall Flume Flow Measurement, Aeration Basin
pHT-6 pHR-6	pH Measurement, Aeration Basin
TR-1 TR-2	Temperature Measurements

FIGURE VIII - 3
ACTIVATED SLUDGE PLANT - 6 MGD
PRETREATMENT AND AERATION


PLANT AMMONIA SYSTEM
LIQUID AMMONIA
PLANT ACID SYSTEM
BASIS: 38% HCl
LV 1
LIC 1
LT 1
D1
38% HCl
SURGE
30,000 GALS
~14.5 GPM
PI 1
FT 1
PHT 1
PHRC 1
TR 1
FEED
4200
GPM
6.70'
6.00'
7.35
6.35'
SUBMERGED SAFETY VALVE VENT
PSV 2
10,000
GAL.
LIQ NH3 STRG.
D2
FT 2
FRC 2
NUTRIENT ADDITION
D4
FT 4
FRC 4
FV 4
NE 5
AT 5
75% H3PO4 STRG.
7,500 GALS.
2.5'
4.2'
8.3'
AERATION
BASIN
EQUALIZATION AND COOLING
POND
~ 60 GPM
FROM THICKENER
~ 16 GPM
FROM CENTRIFUGES
~ 1040 GPM SLUDGE RECYCLE
ARC 2
DILUTION
WATER SUPPLY
~450 GPM
80% SEA WTR
~350 GPM
FRESH WTR
EXCESS SLUDGE
TO THICKENER
~ 80 GPM
8,000 PPM - VSS
EFFLUENT
~4,200 GPM
6.7'
3'
CL
CLARIFIER
75' DIA X 6' DEEP

average temperature is 85°F., requires a pond containing 264,800 square feet of surface area. For a retention time of 2 days, necessary for the equalization of the concentration of organics in the feed, the volume of the pond would be 1.6 x 10^6 cubic feet. The depth of the pond as designed is 7.35 feet, with a freeboard of 1 foot when full. The pond is lined with 0.03 inch thick plastic film. The layout and a cross-section of the pond are shown in Figures VIII-2 and VIII-3, respectively.

Nutrient Addition

Nutrients are added to the aeration basin rather than to the feed in the cooling pond to prevent any anaerobic growth in the pond. Anhydrous ammonia is pumped from a 10,000 gallon storage tank at a rate of 0.366 gpm. Phosphoric acid, 75%, is pumped from a 7,500 gallon storage tank at a rate of 0.05 gpm. The ratio of TOD removed:N:P in the aeration basin will then be 300:10:1.

Dilution Water

The water lost by evaporation in the cooling pond is replaced by the addition of river water (or seawater at coastal locations), to keep the salt content of the feed at about 9%. This addition has the added advantage of supplying any trace elements required for the growth of the bacteria not present in the glycol wastewater. The requirement for fresh water is about 355 gpm.; estuarine water of 2.5% salt content if used instead should be added at a rate of 480 gpm. Alternatively, the ammonia and phosphoric acid could be mixed with the dilution water before addition to the aeration basin, and the dilution water can also be delivered through foam control jets placed at the surface of the aeration basin should foaming become a problem.

Aeration Basin

The aeration basin is designed as a completely mixed reactor, with a residence time of 9.86 hours based on the feed rate. The volume of the basin is 300,000 cubic feet with a depth of 15 feet and a freeboard of 2.5 feet when running full.

The feed flows by gravity from the cooling pond through a 3 foot by 3 foot Parshall flume installed in the common levee between the two basins (Figures VIII-2 and VIII-3).

The oxygen required for the removal of 67,200 pounds TOD per day is calculated as 2070 pounds oxygen per hour. This oxygen is supplied by nine 75 H.P. floating surface aerators. The energy delivered is more than that required to keep the basin completely mixed. The bottom of the basin is lined with a 30 mil plastic film and a concrete base is installed under each surface aerator. Details of the aeration basin are shown in Figure VIII-4.

The suspended solids would be maintained at 1500 ppm. throughout the completely mixed basin. The recycle of 25% of the feed is more than is required to return an adequate quantity of the compacted sludge. The designed organic loading in the basin is 2.28 pounds TOD removed per pound of MLVSS.

Clarifier and Return Sludge

A Dorr-Oliver type clarifier with vacuum pick-up raker arms is used. The clarifier is 75 feet in diameter with an effective depth of 6 feet. It is designed for an overflow rate of 1370 gallons per day per square foot, and a residence time of 47 minutes. The sludge recycled to the aeration basin is 25% of the feed rate, about 1040 gallons per minute and contains about 7,000 ppm. of suspended solids.

Sludge Thickening and Centrifuging

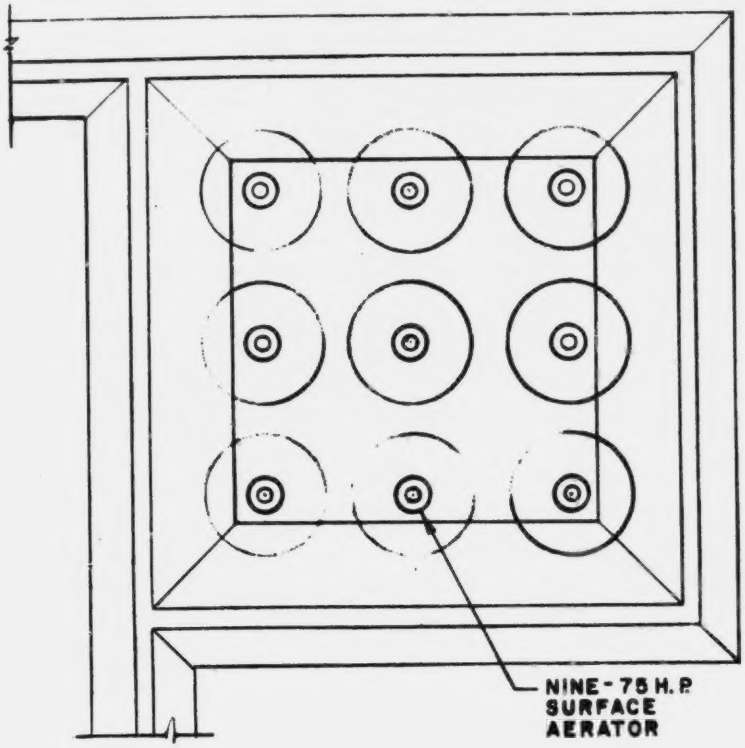
The excess sludge is pumped from the clarifier at a rate of 92 gpm. to a sludge thickener. The thickener is 18 feet in diameter and 6 feet deep, designed for an overflow rate of 400 gallons per day per square foot and a residence time of 2 hours. The sludge is compacted by settling to a volume of 20 gallons containing 3.2% solids, and is pumped to two Dorr-Oliver type centrifuges (Model 12-L) with 25 H.P. motors. The thickened sludge is centrifuged to 18% solids and removed to land fill. The supernatants from both the thickener and centrifuges are pumped to the aeration basin. The details of the sludge handling are shown in Figure VIII-5.

B. Cost Estimate and Economic Evaluation

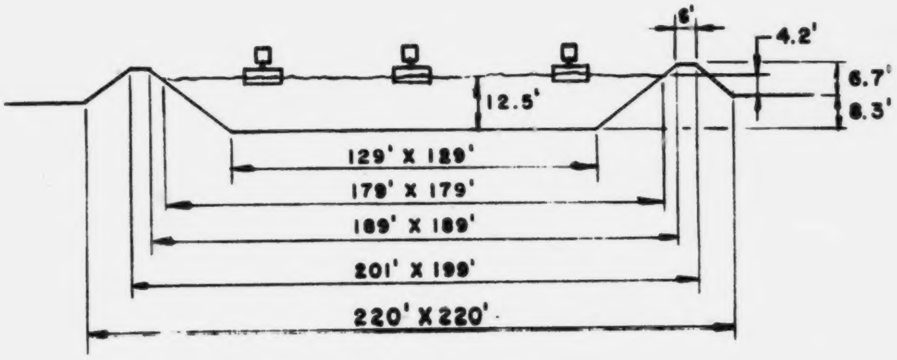
The activated sludge plant requires a total area of about 11.0 acres. The capital and operating costs estimated are confined to the block line. Not included are any items that vary with the location site:

1. Cost of land site, 11.0 acres.
2. Cost of pipeline from glycol production plant to the block line.
3. Cost of transfer of the treated waste from the block line to a disposal or reuse point.
4. Cost of disposing of the centrifuged excess sludge to a land fill location.

FIGURE VIII-4
ACTIVATED SLUDGE PLANT-6 MGD DETAILS OF AERATION BASIN

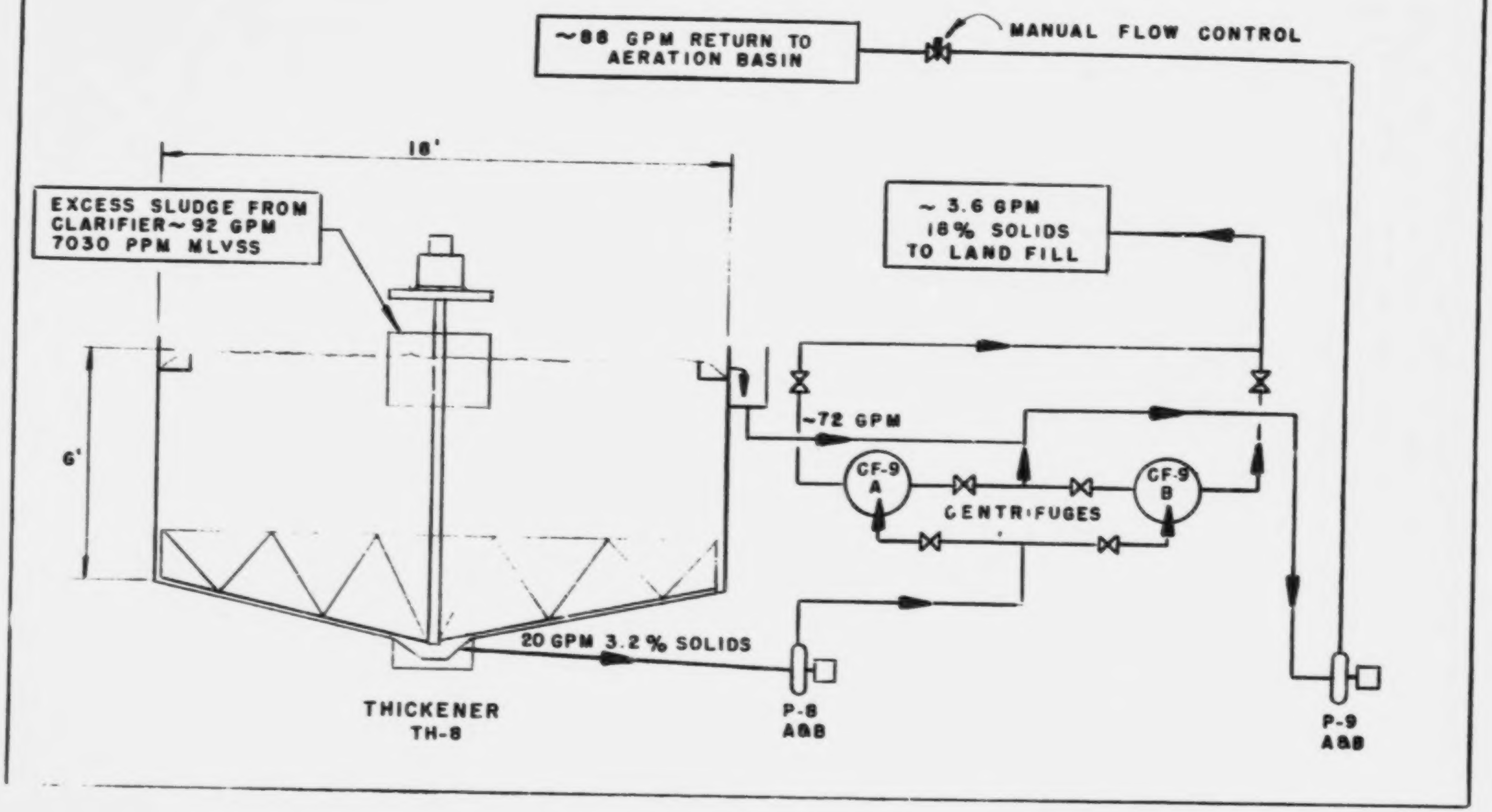

NINE-75 H.P. SURFACE AERATOR

PLAN


6'
4.2'
6.7'
8.3'
12.5'
129' X 129'
179' X 179'
189' X 189'
201' X 199'
220' X 220'

CROSS SECTION

FIGURE VIII-5
ACTIVATED SLUDGE PLANT - 6 MGD
SLUDGE HANDLING


~88 GPM RETURN TO AERATION BASIN
MANUAL FLOW CONTROL
18'
EXCESS SLUDGE FROM CLARIFIER ~ 92 GPM 7030 PPM MLVSS
~ 3.6 GPM 18% SOLIDS TO LAND FILL
6'
~72 GPM
CF-9 A
CF-9 B
CENTRIFUGES
20 GPM 3.2 % SOLIDS
THICKENER TH-8
P-8 A&B
P-9 A&B

The capital cost estimated includes installation cost plus contractor fee and overhead, to which is added 15% allowances each for engineering and contingencies. The details of the derivation of the installed cost of each of the equipment items and services are given in Appendix D.

A listing of the direct capital equipment is given in Table VIII-4. Sub-totals are shown for the pretreatment section of the plant, the aeration and settling section, the sludge handling section and the general services.

The total direct capital cost would be increased to about 1.39 million dollars after allocation of capital for utilities and factory expenses as shown in Table VIII-5.

An estimate of the operating cost is shown in Table VIII-6. The major operating cost item is the acid used to neutralize the excess alkalinity in the wastewater. A reduction in the excess alkalinity by better control at the production plant and a possible lower cost of the acid at the production facilities could amount to a saving of up to half of the estimated operating cost.

The unit cost based on the oxygen demand removed from the wastewater is 3.23 cents per pound of TOD removed. If based on the glycol production, the cost is less than 0.2 cents per pound of glycol produced.

TABLE VIII-4

6 MGD ACTIVATED SLUDGE WASTE TREATMENT PLANT
ESTIMATE OF DIRECT CAPITAL COST

Items	Installed Capital Cost
1. **Pretreatment and Cooling**	
38% HCl Tank	$ 27,100
38% Pumps	6,180
Equalization & Cooling Pond	211,550
Ammonia Storage Tank	40,500
Phosphoric Acid Storage Tank	23,600
Phosphoric Acid Pumps	6,540
Dilution Water Pumps	10,060
Total	$ 325,530
2. **Aeration and Settling**	
Aeration Basin & 9, 75 H.P. Surface Aerators	$ 214,000
Clarifier	239,980
Sludge Recycle Pumps	21,600
Recycle Pumps from Thickener & Centrifuges	9,930
Total	$ 485,510
3. **Sludge Handling**	
Thickener	$ 56,400
Sludge Pumps to Centrifuges	3,460
Centrifuges	141,000
Total	$ 200,860

Table VIII-4 (Continued)

Items	Installed Capital Cost
4. General Services	
Office, Laboratory, Instrument Rm. & Shop	$ 109,000
Instrument Air	11,700
Instrumentation (installed)	59,600
Roads and Parking	40,300
Total	$ 220,600
TOTAL DIRECT CAPITAL COST	$ 1,232,500

TABLE VIII-5

6 MGD ACTIVATED SLUDGE WASTE TREATMENT PLANT COMPUTATION OF FIXED CAPITAL

Item	Units	Units/Year	Capital $/Unit/Yr	Capital
Direct Capital				$1,232,500
Allocated Capital				
Electric Power	KWH	6.52×10^6	0.008	54,000
Riverwater, untreated	MGals	1.9×10^5	0.100	19,000
Factory Expenses				
7% of Direct Capital				86,300
TOTAL FIXED CAPITAL				$1,391,800

TABLE VIII-6

6 MGD ACTIVATED SLUDGE WASTE TREATMENT PLANT ESTIMATE OF OPERATING COST

Cost Items	Quantity Units/Yr.	Units	Cost \$/Unit	Cost \$/Year
Raw Materials				
HCl, 38% solution	2.87×10^7	Lbs.	0.015	\$431,000
H_3PO_4, 75% solution	3.47×10^5	Lbs.	0.0695	24,100
Liquid Ammonia	9.65×10^5	Lbs.	0.032	30,900
Operating Labor (4 man-yrs.)				54,000
Maintenance	6% of Process Equip. Capital			49,800
Power	6.52×10^6	KWH	0.0054	35,200
Untreated River Water	1.9×10^5	MGals	0.0145	2,800
Factory Expense	2.6% of Direct Capital			31,700
Taxes and Insurance	1.1% of Direct Capital			13,400
Depreciation				
Site preparation, Ponds and Buildings	\$402,500 at 5% per year			20,100
Process Equipment	\$830,000 at 10% per year			83,000
TOTAL OPERATING COST				\$775,000

TOD removed per year = 2.4×10^7 lbs.

Cost per pound TOD removed = \$ 0.0323

Propylene glycol production = 4.38×10^8 lbs./yr.

Cost per pound propylene glycol produced = \$ 0.00177

SECTION IX

ACKNOWLEDGMENTS

The work reported was performed at the Texas Division of The Dow Chemical Company by Dr. M. A. Zeitoun, the principal investigator, C. A. Roorda, J. C. Williams, R. W. Murray, and W. D. Spears. W. F. McIlhenny was the Project Director. Dr. W. A. Taber of Texas A. & M. University was a consultant on the microbiology and holder of a subgrant.

The project was partially supported by a Class V Research, Development and Demonstration Grant from the Office of Research and Monitoring, Environmental Protection Agency. The advice and assistance of the following personnel connected with the granting agency is gratefully acknowledged: Lawrence Lively and Frank Mayhew of the Robert S. Kerr Water Quality Research Center, Ada, Oklahoma and George Rey and W. J. Lacy of the Applied Science and Technology Branch, Technology Division, Washington, D. C.

A special acknowledgment is due to James A. Horn, the EPA Project Officer in Ada, Oklahoma, whose advice was invaluable throughout the project and who reviewed the final manuscript.

SECTION X

REFERENCES

Bergey's Manual of Determinative Bacteriology, 7th Edition, Williams and Wilkins Co., Baltimore.

Bhatla, M. N., V. T. Stack and R. F. Weston. "Design of Wastewater Treatment Plants from Laboratory Data", JWPCF, Vol. 38, No. 4, pp. 601-613. (1966).

Busch, A. W. "Process Kinetics as Design Criteria for Biooxidation of Petrochemical Wastes", J. of Engineering for Industry. (May 1963).

Davison, R. R., W. H. Smith, Jr. and D. W. Hood. "Structure and Amine Water Solubility in Desalination by Solvent Extraction", Jour. Chem. and Eng. Data, Vol. 5, No. 4, p. 420. (1960).

Dickenson, R. L. and J. L. Giboney. "Stabilization of Refinery Wastewaters with the Activated Sludge Process: Determination of Design Parameters", paper presented at the 25th Purdue Industrial Waste Conference, Lafayette, Indiana. (May 1970).

Eckenfelder, W. W., Jr. and D. J. O'Connor. "Biological Waste Treatment", The Macmillan Company, New York. (1961).

Ford, D. L. and W. Jewell. "Preliminary Investigational Requirements--Petrochemical and Refinery Waste Treatment Facilities", Report No. 12020 EID 02/71, Environmental Protection Agency. (January 1971).

FWPCA, Robert S. Kerr Water Research Center. "Laboratory Quality Control Manual". (1969).

Hatfield, R. "Biological Oxidation of Some Organic Compounds", Industrial Engineering Chemistry, Vol. 49, p. 192. (1957).

Ludzack, F. J. and D. K. Noran. "Tolerance of High Salinities by Conventional Wastewater Treatment Processes", JWPCF, Vol. 37, No. 10, pp. 1404-1416. (1965).

Marian, C. V. and G. W. Maloney. "The Oxidation of Aliphatic Compounds by Alcaligenes Faecalis", JWPCF, Vol. 35, p. 1269. (1963).

Preceding page blank

Mills, E. J. and V. T. Stack. "Biological Oxidation of Synthetic Organic Chemicals", Proceedings, 8th Industrial Waste Conference, Purdue University, Extension Series No. 83, p. 492. (1954).

Mulbarger, M. C. and J. A. Castelli. "A Versatile Activated Sludge Pilot Plant--Its Design, Construction and Operation", Proceedings, 21st Waste Conference, Purdue University, Extension Series No. 121, pp. 322-337. (1966).

Placak, O. R. and C. C. Ruchholt. "Studies in Sewage Purification, XVII. The Utilization of Organic Substrates by Activated Sludge", Sewage Works Journal, Vol. 19, p. 423. (1947).

Sourirajan, S. and S. Kimura. I.E.C. 6, Proc. Design Develop., No. 4, p. 504. (October 1967).

Symons, J. M., R. E. McKinney and H. H. Hassis. JWPCF, pp. 841-851. (August 19 0).

Yuzaburo Ishida and Tateo Fuji. "Isolation of Halophilic and Halotolerant Bacteria from Solar Salt", Bulletin of the Japanese Society of Scientific Fisheries, Vol. 36, No. 4. (1970).

Zeitoun, M. A. and R. R. Davison. "Clean Water by Extraction", Chem. Eng. Progress, Vol. 60, No. 12, pp. 51-54. (1964).

SECTION XI

APPENDICES

		Page
Appendix A	Development of Analytical Methods	138
Appendix B	Activated Sludge Pilot Plant Operation	145
Appendix C	Characteristics of Bacteria From the Activated Sludge Pilot Plant	160
Appendix D	Design Calculations and Cost Estimates of a 6 MGD Activated Sludge Plant	166
Appendix E	Microbial Metabolism of Ethylene and Propylene Glycols in Presence of Sodium Chloride. "Abstract" by Dr. W. A. Taber	198

Appendix A. Development of Analytical Methods

Standard analytical procedures were used for the routine analyses of % NaCl, total dissolved solids (TDS), pH, excess alkalinity as NaOH, and specific gravity. Trace metal ions in a typical waste stream were measured by emission spectroscopy. Periodic analyses of added nutrients included total nitrogen by Kjeldahl, ammonia nitrogen by Nesserization and total phosphorus by the stannous chloride method.

The analyses of the organic constitutents of petrochemical wastewaters are more difficult to perform and to interpret. The characterization of the organic content of the wastewater resulting from the production of ethylene and propylene glycols required the development of gas chromatographic methods to identify the organic components. There are many limitations of the standard methods of characterizing wastes such as BOD and COD. The instrumental methods that determine total organic carbon (TOC) and total oxygen demand (TOD) were found to be more effective than BOD and COD for correlation of the laboratory and pilot plant data.

Chemical Oxygen Demand (COD)

The standard dichromate COD test was found to be unsuitable because of the very high concentration of chloride ion in the waste stream. The 2-hour permanganate COD test was used instead and yielded values slightly lower than the instrumental TOD values.

Biochemical Oxygen Demand (BOD)

The standard 5-day BOD test was conducted on samples of the waste streams using a sewage seed acclimated for at least three days to the diluted waste. Biological oxidation over a 10-day period was determined in BOD bottles with solutions of the organic components known to be present in the waste streams. Solutions containing 100 ppm. of each compound were prepared and diluted 15 times in the BOD bottles and 1 ml. of an acclimated sewage sludge seed was added to each of 10 bottles for each compound tested. A seed from the treatability tests that had been acclimated to the actual waste over a period of two months was also used to determine the 10-day biological oxidation curve for the organic components of the waste stream.

Total Oxygen Demand (TOD)

A Dow-TOD analyzer was used for the analyses of the total oxygen demand of the waste samples. A micro sample is injected into a catalytic combustion tube enclosed by an electric furnace thermostated at 900°C. A carrier gas of nitrogen containing about 200 ppm. oxygen flows through a caustic scrubber to an oxygen silver-lead fuel cell. The amount of oxygen consumed by the sample is directly proportional to the concentration of the oxygen demanding organics in the sample. The wastewater from the glycol production contains no nitrogeneous organics that would interfere. This analytical method was adopted as the principal measure of the organic content of the raw and processed wastewaters.

Total Organic Carbon (TOC)

A Dow-Beckman Carbonaceous Analyzer was acquired during the operation of the activated sludge pilot plant and used for the analyses of the process streams. The method entails the injection of a micro sample into a catalytic combustion tube at 950°C. The carbonaceous material is oxidized to carbon dioxide in a carrier stream of pure oxygen. The amount of CO_2 produced is directly proportional to the amount of carbonaceous material in the injected sample and is measured by a sensitized infrared analyzer. Samples were acidified and stripped with nitrogen gas blown through to free the sample from inorganic carbon before injection into the TOC instrument.

Organic Components by Vapor Phase Chromatography (VPC)

A two-column, two detector, VPC unit was purchased from the Antek Company of Houston, Texas. The main column used is a 1/8-inch stainless steel thin wall, 36 inches long, packed with Purapak Q (available from Waters Associates) plus 15% by weight of E-20,000 (polyethylene glycol, average molecular weight 20,000). The column temperature is maintained at about 150°C. and the hydrogen-air flame ionization detector at about 180°C. Helium is used as the carrier gas at a flow rate of 60 to 80 milliliters per minute.

This column was capable of separating all of the five principal components in the hydrolyzer wastewater except the ether which has the longest retention time. Another 24-inch long column packed with 25% by weight of the liquid phase E-20,000, and using a 30 ml./minute carrier gas flow rate, was used to separate the ether.

The VPC analysis of a mixture of ethylene glycol and propylene glycol required a more polar column for the separation of the two glycols. A 5-foot, 1/8-inch column packed with 120-150 mesh Purapak Q, without any liquid phase, was used successfully to separate the two glycols and their corresponding chlorohydrins. The column packing had to be replaced once a month as it loses its polarity with time.

Glycol Analysis by Periodate Oxidation

This method of analysis is specific for glycols having hydroxyls on adjacent carbons. The oxide and the chlorohydrin are also detected if hydrolyzed to the glycol in acid solution prior to the periodate oxidation test.

A 10 ml. aliquot of the diluted sample is reacted with 50 ml. of 0.4 N sodium periodate ($NaIO_4$) solution for 1 hour. The reaction mixture is diluted with 150 ml. distilled water, followed by 20 ml. of 20% sulfuric acid and 40 ml. of 30% potassium iodide solution. The reaction mixture is then titrated with standardized 0.2 N sodium thiosulfate using 2 ml. of starch solution as a final indicator. A reagent blank is run concurrently and the percent glycol in the sample is calculated from the difference between the blank and the sample titrations.

Total Suspended and Volatile Suspended Matter

The wastewater contains negligible amounts of suspended matter (less than 10 mg./l.). The mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS), were determined using a millipore filtering apparatus. A comparison of the use of a 0.45μ millipore filter and a Gooch crucible is given in Table XI-1.

The variation in the MLSS is higher than the MLVSS due to the error introduced by the washing of the salt content on the filter paper. The MLVSS values are more reliable, and duplicates agree better than do the MLSS values.

Dissolved Oxygen

Measurements of dissolved oxygen (DO) in the samples from the activated sludge mixed liquor were made using a YSI model 51A oxygen analyzer. The instrument was calibrated against the azide-alum flocculation modification of the Winkler analysis and this calibration, at the saturation oxygen concentration, was used to apply the corrections for the chloride ion concentration in the samples.

The temperature calibration of the instrument was checked daily with distilled water exposed to water-saturated air. Gentle swirling of the probe was found necessary to obtain consistent oxygen readings. High readings could be due to air bubbles sticking on the membrane surface of the probe, and low readings could result from a liquid film depleted of oxygen at the membrane surface.

TABLE XI-1

DETERMINATION OF SUSPENDED SOLIDS
COMPARISON OF METHODS

Sample No.	Mixed Liquor Suspended Solids		Mixed Liquor Volatile Suspended Solids	
	Gooch	Millipore	Gooch	Millipore
1	1283	1250	1109	1033
2	2004	1824	1709	1484
3	2374	2452	2150	2193
4	2719	2606	2467	2402

All values in milligrams per liter, triplicate average.

Quality Control of Laboratory Analyses

A quality control program was initiated during the first few months of this investigation. The total oxygen demand (TOD) and the glycol concentration by gas chromatography were the two main analyses checked daily against precision charts. Twenty duplicate pairs of each analysis were used to construct precision control charts (FWPCA-1969). Figures XI-1 and XI-2 show these charts for the TOD and glycol by VPC analysis, respectively. Based on the initial twenty pairs of samples, a standard deviation of 27 mg./l. of glycol was determined for the VPC analysis, and of 40 mg./l. for the TOD instrument. Results of duplicate samples plotted as cumulative squared differences indicated more precision than the original 20 duplicates used to construct the chart.

Accuracy control charts for TOD and glycol by VPC were also constructed from a set of sixteen standard solutions prepared by the Central Laboratories of the Texas Division of The Dow Chemical Company. The upper and lower limits of the accuracy charts are:

TOD accuracy chart; $S_d = 99$ mg./l.

$$\text{U.L. } (M) = 50 \times 10^3 + 9.2 \times 10^3 \ (M)$$

$$\text{L.L. } (M) = -50 \times 10^3 + 9.2 \times 10^3 \ (M)$$

Glycol, VPC accuracy chart; $S_d = 43$ mg./l.

$$\text{U.L. } (M) = 9.4 \times 10^3 + 1.74 \times 10^3 \ (M)$$

$$\text{L.L. } (M) = -9.4 \times 10^3 + 1.74 \times 10^3 \ (M)$$

The quality control program is believed to have served two important purposes. First, it created an atmosphere of awareness among the analysts, and secondly, it increased our confidence in the numbers generated by the analytical methods used.

Figure XI-1

PRECISION CONTROL CHART – TOD ANALYSIS
RANGE 50–2500 mg/l

Nov. 18, 1969

$\alpha = 0.1$ $\beta = 0.1$ $S_d = 40$ mg/l TOD

$UL = 158 \times 10^3 + 29 \times 10^3 (M)$
$LL = -158 \times 10^3 + 29 \times 10^3 (M)$

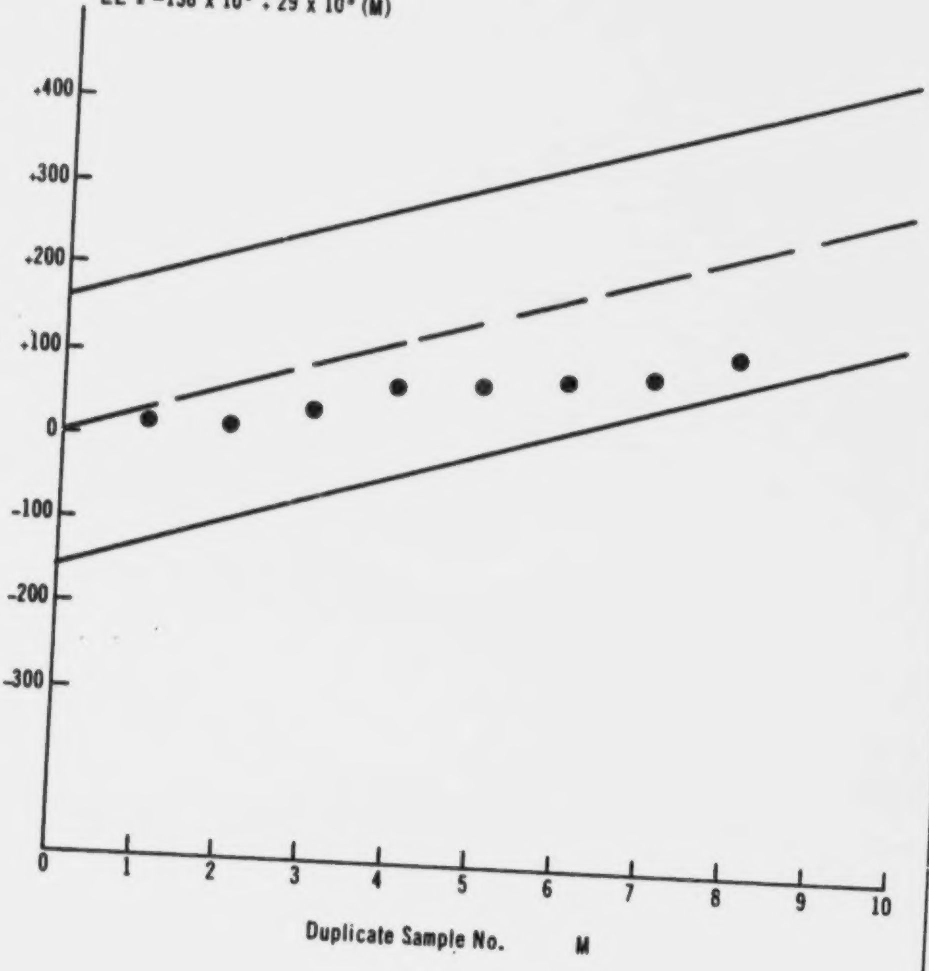
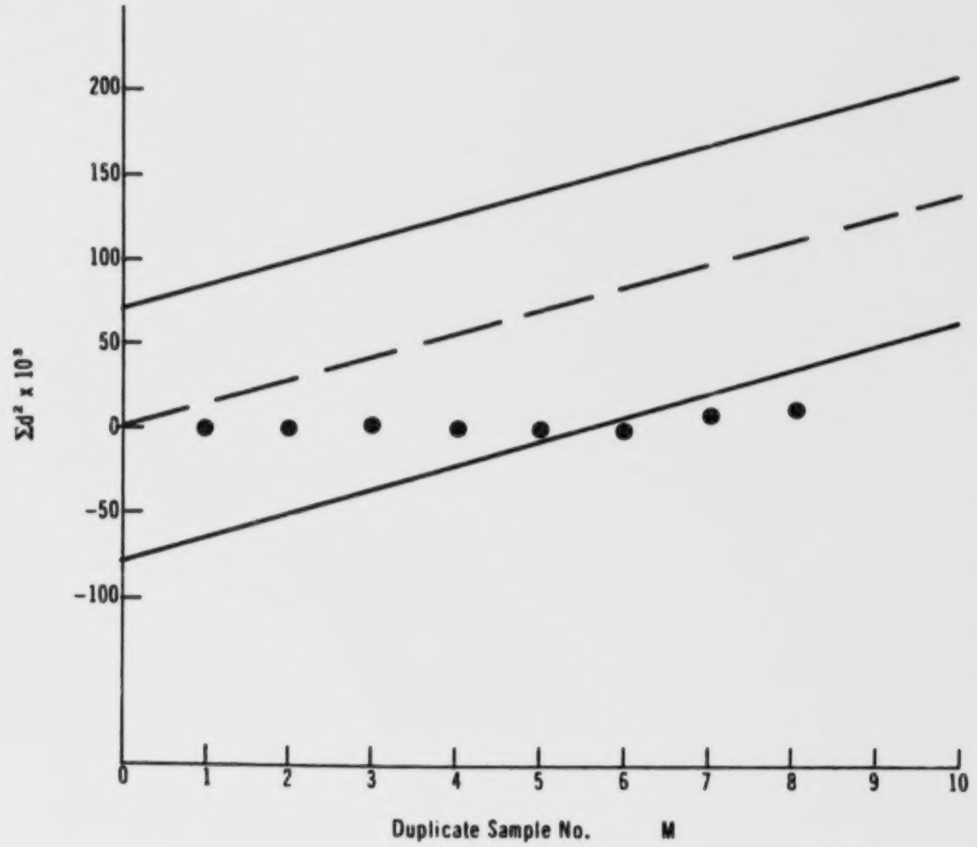


Figure XI-2

PRECISION CONTROL CHART – GLYCOL VPC ANALYSIS
RANGE 200–2000 mg/l

Dec. 7, 1969
$\alpha = 0.1$ $\beta = 0.1$ $S_d = 27.0$ mg/l glycol

$UL = 73.8 \times 10^3 + 13.6 \times 10^3 (M)$
$LL = -73.8 \times 10^3 + 13.6 \times 10^3 (M)$



Appendix B. Activated Sludge Pilot Plant Operation

The detailed analytical results and daily measured and derived values obtained during pilot plant operation are tabulated in this appendix. Three operating periods, June 24 to August 27, 1970, September 10 to November 6, 1970, and November 20 to December 28, 1970, are given in Tables XI-2, XI-3, and XI-4, respectively. The nearly steady state operation of the plant under controlled conditions, from December 29, 1970 to February 28, 1971, is given in Table XI-5.

TABLE XI-2

PILOT PLANT OPERATION
MIXED PG AND EG WASTEWATERS - PLUG FLOW REACTOR

Date	Pretreated Feed			Effluent from Aeration			Flocculated Effluent		TOD Removal %	Flow Rate gals./min.
	NaCl %	Glycols ppm	TOD ppm	MLVSS ppm	Glycols ppm	TOD ppm	Glycols ppm	TOD ppm		
June 24	8.9	550	1700	1320	60	760	60	350	80	0.210
June 25	9.5	490	1200	1460	70	730	100	600	50	0.205
June 26	9.4	510	1420	1350	80	640	40	460	68	0.160
June 27	9.6	610	1550	1570	40	650	40	440	72	0.160
June 28	9.7	590	1760	1260	20	320	20	320	81	0.160
June 29	8.8	630	1800	1350	20	570	20	380	79	0.160
June 30	9.3	430	1260	530	20	480	20	280	78	0.242
July 1	9.7	580	1760	1410	20	600	20	220	87	0.160
July 2	10.0	430	1380	1450	20	420	20	200	85	0.275
July 3	8.5	370	1290	1520	20	360	20	230	82	0.270
July 4	10.2	630	1640	1920	-	-	20	200	88	0.270
July 5	9.9	500	1740	1540	-	-	20	180	90	0.270
July 6	9.0	525	1760	1330	20	410	20	160	91	0.265
July 7	Loss of culture due to leakage - Aeration tank filled with secondary culture									
July 8	9.1	550	1210	600	20	235	20	165	86	0.160
July 9	10.1	550	1530	680	20	350	20	220	86	0.300
July 10	10.6	420	1380	1080	20	270	20	150	89	0.290
July 11	10.4	470	1440	1260	-	-	20	150	90	0.300

Table XI-2 (Continued)

Date	Pretreated Feed NaCl %	Pretreated Feed Glycols ppm	Pretreated Feed TOD ppm	Effluent from Aeration MLVSS ppm	Effluent from Aeration Glycols ppm	Effluent from Aeration TOD ppm	Flocculated Effluent Glycols ppm	Flocculated Effluent TOD ppm	TOD Removal %	Flow Rate gals./min.
July 12	10.4	340	1220	1860	-	300	20	120	90	0.300
July 13	9.0	470	1320	1150	20	220	20	100	92	0.300
July 14	10.0	540	1820	1260	20	330	20	160	91	0.300
July 15	9.8	500	1650	1300	20	330	20	160	90	0.300
July 16	8.7	540	1720	1700	20	350	20	115	93	0.300
July 17	9.3	540	1390	1770	20	380	20	150	89	0.300
July 18	10.2	690	1260	600	20	320	20	130	89	0.300
July 19	10.2	590	1500	900	20	550	20	230	85	0.300
July 20	10.1	600	1710	260	20	450	20	230	86	0.300
July 21	10.2	570	1500	1320	20	570	20	160	89	0.300
July 22	Shut-down due to short circuit caused by excess foam leaking on wiring									
July 23	9.4	790	1920	1290	180	1000	160	230	88	0.300
July 24	9.9	-	1550	1780	140	860	140	260	84	0.300
July 25	9.6	-	1850	1970	-	-	60	165	91	0.300
July 26	9.7	-	1810	1770	-	-	20	100	94	0.300
July 27	9.5	810	1630	1860	-	490	20	140	92	0.300
July 28	9.1	550	1300	1800	20	380	20	120	91	0.300
July 29	9.9	570	1300	1790	20	310	20	120	91	0.300
July 30	9.9	750	1600	1700	20	260	20	80	95	0.300
July 31	10.2	940(1)	2000	2310	20	210	20	70	95	0.300

Date	Pretreated Feed			Effluent from Aeration			Flocculated Effluent		TOD Removal	Flow Rate
	NaCl %	Glycols ppm	TOD ppm	MLVSS ppm	Glycols ppm	TOD ppm	Glycols ppm	TOD ppm	%	gals./min.
Aug. 1	10.1	1020 (1)	1980	2450	-	-	20	100	95	0.300
Aug. 2 (2)	-	1270 (1)	1950	440	-	-	20	180	90	0.300
Aug. 3	9.9	1120 (1)	1800	-	150	720	140	420	66	0.300
Aug. 4	9.5	920 (1)	1750	1700	180	810	110	540	64	0.300
Aug. 5	9.5	650	1570	1290	250	860	260	520	57	0.300
Aug. 6	9.7	690	1330	1450	90	440	120	350	70	0.300
Aug. 7	10.3	870	1600	1300	50	220	70	130	90	0.300
Aug. 8	10.0	715	1420	1230	-	-	60	200	84	0.300
Aug. 9	10.0	540	1130	800	-	-	100	340	68	0.300
Aug. 10 (3)	10.0	600	1400	1900	240	460	220	360	74	0.300
Aug. 11	10.2	530	1420	1220	130	290	110	220	84	0.300
Aug. 12	10.2	790	1370	1320	20	130	20	70	95	0.30C
Aug. 13	10.0	750	1860	1170	40	250	30	220	86	0.300
Aug. 14	10.5	820	1370	1590	35	200	25	120	91	0.300
Aug. 15	10.[illegible]	700	1430	1520	50	370	20	100	92	0.300
Aug. 16-										
Aug. 17	Repair pH control - Batch feeding of aeration tank									
Aug. 18-										
Aug. 19	10.5	670	1420	2020	20	360	20	240	83	0.300
Aug. 20	10.[illegible]	420	1280	1700	20	380	20	150	90	0.300

Table XI-2 (Continued)

Date	Pretreated Feed NaCl %	Pretreated Feed Glycols ppm	Pretreated Feed TOD ppm	Effluent from Aeration MLVSS ppm	Effluent from Aeration Glycols ppm	Effluent from Aeration TOD ppm	Flocculated Effluent Glycols ppm	Flocculated Effluent TOD ppm	TOD Removal %	Flow Rate gals./min.
Aug. 21	10.2	630	1480	2400	20	490	20	160	90	0.300
Aug. 22	9.9	770	1500	830	-	-	20	150	91	0.400
Aug. 23(3)	9.7	840	1410	1180	20	300	20	140	90	0.400
Aug. 24	10.0	360	1250	2200	20	450	20	150	88	0.400
Aug. 25	8.8	740	1690	1480	20	300	20	120	91	0.400
Aug. 26	9.1	900	1490	-	160	550	180	290	80	0.400
Aug. 27 to Sept. 9	Major repairs of feed pump, overflow piping from aeration tank. Remove partitions and connect HCl acid tank to the neutralizing system.									

(1) Propylene glycol feed.

(2) Feed from production plant cut off most of the day. Secondary culture added.

(3) Secondary culture added.

TABLE XI-3

PILOT PLANT OPERATION
PROPYLENE GLYCOL WASTE - COMPLETELY MIXED REACTOR

Date	Pretreated Feed NaCl %	Pretreated Feed Glycols ppm	Pretreated Feed TOD ppm	Effluent from Aeration MLVSS ppm	Effluent from Aeration Glycols ppm	Effluent from Aeration TOD ppm	Flocculated Effluent Glycols ppm	Flocculated Effluent TOD ppm	TOD Removal %	Flow Rate gals./min.
Sept. 10	9.3	940	2900	350	420	800	310	620	71	0.325
Sept. 11	9.6	1240	2090	520	550	680	550	580	72	0.325
Sept. 12	9.7	1060	2200	990	-	-	420	500	77	0.325
Sept. 13	10.1	720	1800	330	320	650	180	420	77	0.325
Sept. 14	10.2	800	1980	360	90	560	110	380	77	
Sept. 15-	Plant shut down to repair leaks and reinforce the structure of the aeration tank									
Sept. 16-										
Sept. 17	10.1	920	2200	560	170	620	60	340	85	0.325
Sept. 18	10.3	770	2430	520	100	530	120	390	84	0.325
Sept. 19	10.1	560	1970	790	60	470	70	370	81	0.325
Sept. 20	9.5	590	1790	780	-	-	20	240	87	0.325
Sept. 21	9.6	520	2060	630	50	500	40	370	82	0.325
Sept. 22	9.8	650	2420	620	40	680	50	420	83	0.325
Sept. 23	10.0	740	1780	460	20	600	20	320	82	0.325
Sept. 24	10.0	650	2050	740	20	370	20	170	91	0.325
Sept. 25	9.9	680	2080	980	20	370	20	130	93	0.325
Sept. 26	9.7	800	2100	820	20	510	20	160	92	0.325
Sept. 27	9.4	580	2260	870	-	-	20	190	92	0.325

Table XI-3 (Continued)

Date	Pretreated Feed			Effluent from Aeration			Flocculated Effluent		TOD Removal	Flow Rate
	NaCl %	Glycols ppm	TOD ppm	MLVSS ppm	Glycols ppm	TOD ppm	Glycols ppm	TOD ppm	%	gals./min.
Sept. 28	9.8	520	2020	690	20	550	20	210	89	0.325
Sept. 29	9.5	570	1980	1060	20	480	20	160	91	0.325
Sept. 30	10.0	860	2060	1280	20	390	20	180	91	0.325
Oct. 1(1)	9.6	930	2400	1360	20	240	20	70	97	0.325
Oct. 2	9.5	940	1940	1200	20	590	20	110	94	0.325
Oct. 3(2)	10.2	1960	3240	320	40	940	80	540	82	0.400
Oct. 4	9.7	700	2170	560	-	-	380	600	70	0.318
Oct. 5	9.8	880	1960	480	300	810	260	480	70	0.318
Oct. 6	9.7	630	2180	-	150	640	200	450	75	0.318
Oct. 7	10.2	820	1980	360	50	470	20	340	83	0.325
Oct. 8	9.7	700	1890	580	190	510	230	500	69	0.325
Oct. 9	9.8	720	2100	310	80	460	70	380	82	0.325
Oct. 10	9.4	840	2140	250	190	540	110	590	72	0.325
Oct. 11	9.5	780	1830	170	-	-	600	570	68	0.325
Oct. 12	9.7	1030	1950	460	850	690	790	590	70	0.325
Oct. 13(3)	9.9	1210	1860	840	-	-	720	540	71	0.325
Oct. 14	8.8	810	1970	510	100	550	190	440	73	0.325
Oct. 15	9.0	820	1930	540	20	420	40	220	88	0.325
Oct. 16	8.9	840	2020	460	30	475	70	270	86	0.325
Oct. 17	9.2	770	2300	240	20	225	40	250	86	0.325
Oct. 18	9.8	860	1970	200	100	600	160	370	81	0.325

Table XI-7 (Continued)

Date	Pretreated Feed			Effluent from Aeration			Flocculated Effluent		TOD Removal	Flow Rate
	NaCl %	Glycols ppm	TOD ppm	MLVSS ppm	Glycols ppm	TOD ppm	Glycols ppm	TOD ppm	%	gals./min.
Oct. 19	9.8	880	2150	380	140	480	190	500	76	0.325
Oct. 20	9.6	790	2040	670	30	430	40	280	86	0.325
Oct. 21	9.6	960	1900	660	20	200	20	190	90	0.325
Oct. 22	9.3	640	1520	910	20	190	20	140	91	0.325
Oct. 23	9.7	870	1820	1190	60	260	20	120	93	0.325
Oct. 24	10.0	1080	2640	1200	-	-	20	150	94	0.325
Oct. 25	9.8	950	2110	1360	40	400	20	220	90	0.325
Oct. 26	9.6	1100	1940	1510	30	370	20	220	88	0.325
Oct. 27	10.1	1000	2170	1660	40	320	20	260	88	0.325
Oct. 28	10.0	960	2840	1380	20	440	20	150	94	0.325
Oct. 29	10.0	620	1910	1220	30	520	20	250	83	0.325
Oct. 30	9.9	840	2300	720	20	360	20	260	89	0.4-0.325
Oct. 31	9.7	790	2410	680	50	690	60	330	78	0.400
Nov. 1	9.4	1100	3180	380	-	660	180	660	75	0.400
Nov. 2	9.7	900	2620	330	490	1680	500	1490	43	0.400
Nov. 3	9.2	975	2210	640	-	-	580	1350	-	0.325
Nov. 4	8.8	710	1990	220	-	-	350	990		0.325
Nov. 5	8.8	460	1730	260	220	840	190	730		0.320

Table XI-3 (Continued)

Date	Pretreated Feed			Effluent from Aeration			Flocculated Effluent		TOD Removal	Flow Rate
	NaCl %	Glycols ppm	TOD ppm	MLVSS ppm	Glycols ppm	TOD ppm	Glycols ppm	TOD ppm	%	gals./min.
Nov. 6	Install a 3000-gallon equalization tank and pipe it to the feed system.									
to	Clean up equipment and acclimate bacteria in the aeration tank being batch									
Nov. 19	fed propylene glycol.									

(1) Feed was cut off for 3 hours. This may explain the very high percent removal.

(2) The cooling tower was plugged, temperature of feed rose to 46°C, accompanied by very high organic loading, resulted in anaerobic conditions and loss of bacteria as it floated on the surface of the settling tank.

(3) Secondary culture added.

TABLE XI-4

PILOT PLANT OPERATION
EQUALIZED PG WASTE - COMPLETELY MIXED REACTOR

Date	Pretreated Feed			Effluent from Aeration			Flocculated Effluent		TOD Removal	Flow Rate
	NaCl %	Glycols ppm	TOD ppm	MLVSS ppm	Glycols ppm	TOD ppm	Glycols ppm	TOD ppm	%	gals./min.
Nov. 20	8.9	560	1640	112	230	600	230	600	63	0.320
Nov. 21	8.9	560	1660	84	300	910	240	660	61	0.320
Nov. 22	8.1	560	1680	152	200	680	250	560	67	0.320
Nov. 23	9.1	540	1700	136	100	560	110	520	69	0.320
Nov. 24	9.0	460	1690	310	80	490	70	440	74	0.320
Nov. 25	9.2	480	1760	310	30	370	30	300	83	0.320
Nov. 26										0.320
Nov. 27(1)	9.1	520	1690	540	20	600	20	270	84	0.320
Nov. 28	8.6	300	1490	870	20	530	20	280	81	0.320
Nov. 29	9.2	300	1350	710	20	710	20	370	72	0.320
Nov. 30	9.2	270	1600	540	20	680	20	440	72	0.320
Dec. 1	9.2	220	1150	680	20	450	20	210	82	0.360
Dec. 2	9.1	650	1370	830	20	540	20	160	88	0.360
Dec. 3	9.2	510	1790	930	20	700	20	400	78	0.400
Dec. 4	9.2	520	1400	950	40	540	20	150	89	0.400
Dec. 5	9.3	500	1520	650	20	530	20	270	82	0.400
Dec. 6	9.2	350	1270	540	20	630	20	225	82	0.400
Dec. 7	9.5	570	1510	790	30	550	20	290	81	0.400

Table XI-4 (Continued)

Date	Pretreated Feed			Effluent from Aeration			Flocculated Effluent		TOD Removal	Flow Rate
	NaCl %	Glycols ppm	TOD ppm	MLVSS ppm	Glycols ppm	TOD ppm	Glycols ppm	TOD ppm	%	gals./min.
Dec. 8	9.5	470	1400	840	30	370	20	200	86	0.400
Dec. 9	9.2	530	1280	920	30	250	20	170	87	0.400
Dec. 10	8.8	280	1240	1000	30	420	20	200	84	0.400
Dec. 11	9.2	470	1140	830	40	290	40	250	78	0.400
Dec. 12	9.0	880	2000	730	30	-	30	280	86	0.400
Dec. 13	9.1	660	1310	720	130	540	110	490	62	0.400
Dec. 14	9.0	600	2035	630	170	680	70	670	67	0.400
Dec. 15(3)	9.1	840	1875	600	330	940	340	820	56	0.400
Dec. 16	8.9	500	1570	740	260	900	200	760	52	0.400
Dec. 17	8.8	470	1520	720	240	880	260	780	49	0.400
Dec. 18	9.0	560	1300	760	180	760	240	520	60	0.400
Dec. 19	8.8	450	1220	670	80	660	120	550	55	0.400
Dec. 20	8.8	460	1520	860	30	430	60	420	72	0.400
Dec. 21	9.0	420	1270	890	20	300	20	260	80	0.400
Dec. 22	8.9	410	1430	970	20	310	20	320	78	0.400
Dec. 23	8.9	450	1320	1270	20	330	20	310	77	0.400
Dec. 24	8.7	440	1180	1140	20	350	20	310	74	0.400
Dec. 25	8.5	340	1100	940	30	300	20	300	73	0.400
Dec. 26	8.3	380	1200	1280	20	260	20	280	76	0.400
Dec. 27	7.9	420	1440	920	30	330	30	290	80	0.400

Table XI-4 (Continued)

Date	Pretreated Feed NaCl %	Pretreated Feed Glycols ppm	Pretreated Feed TOD ppm	Effluent from Aeration MLVSS ppm	Effluent from Aeration Glycols ppm	Effluent from Aeration TOD ppm	Flocculated Effluent Glycols ppm	Flocculated Effluent TOD ppm	TOD Removal %	Flow Rate gals./min.
Dec. 28	7.9	420	1370	1640	20	300	20	270	80	0.400

(1) 48-hour samples

(2) Roughing column removing 15-35% of TOD from feed from 11-27 to 12-14.

(3) The feed before equalizing had over 2400 ppm TOD. A cold spell lowered the temperature of the ffed to below 70°F. The roughing column was not operating.

TABLE XI-5

PILOT PLANT OPERATION
EQUALIZED PG WASTE - COMPLETELY MIXED REACTOR

Date	Pretreated Feed			Effluent From Aeration Tank			Flocculated Effluent		TOD Removal %	Flow Rate GPM
	NaCl %	Glycols ppm	TOD ppm	MLVSS ppm	Glycols ppm	TOD ppm	Glycols ppm	TOD ppm		
Dec. 29	8.5	420	1340	1480	20	270	20	280	79	0.400
Dec. 30	8.5	370		1670	20		20			0.400
Dec. 31	8.4	360		2010	20		20			0.400
Jan. 1	8.6	350	1310	1880	40	340	40	270	79	0.400
Jan. 2	7.9	335	1240	2030	20	300	20	240	81	0.400
Jan. 3	7.9	340	1130	2030	20	310	20	270	79	0.400
Jan. 4	7.9	360	1090	2100	20	300	20	280	74	0.400
Jan. 5	8.4	420	1220	2040	30	300	30	180	85	0.400
Jan. 6	8.5	350	1150	1760	20	310	20	160	86	0.400
Jan. 7	8.0	390	1180	1780	20	340	20	230	80	0.400
Jan. 8	8.3	340	1220	1390	20	320	20	250	79	0.400
Jan. 9	8.3	370	1280	1120	20	730	15	490	61	0.400
Jan. 10	8.8	360	1310	960	20	960	20	480	63	0.400
Jan. 11	8.6	350	1270	650	20	620	10	420	67	0.400
Jan. 12				1080	20	440	10	330	73	0.400
Jan. 13	8.3	290	1310	1010	20	390	10	280	78	0.400
Jan. 14	8.5	350	1230	1460	20	300	20	230	81	0.400
Jan. 15	8.5	320	1210	1230	20	350	20	230	81	0.400

Table XI-5 (Continued)

Date	Pretreated Feed			Effluent From Aeration Tank			Flocculated Effluent		TOD Removal	Flow Rate
	NaCl %	Glycols ppm	TOD ppm	MLVSS ppm	Glycols ppm	TOD ppm	Glycols ppm	TOD ppm	%	GPM
Jan. 16	8.7	360	1260	1100	20	310	10	140	89	0.400
Jan. 17	8.8	410	1250	1040	20	310	10	140	89	0.400
Jan. 18	8.6	330	970	800	10	250	10	100	90	0.400
Jan. 19	8.7	360	1080	1100	30	190	10	50	95	0.400
Jan. 20	8.6	340	1130	1150	10	130	10	110	90	0.400
Jan. 21	8.6	390	1170	1160	10	160	10	110	90	0.400
Jan. 22	8.7	380	1200	1020	10	260	10	170	86	0.400
Jan. 23	9.4	400	1280	1320	5	280	5	130	90	0.400
Jan. 24	9.9	450	1300	1480	10	230	10	150	89	0.400
Jan. 25	9.8	410	1190	1580	5	220	5	100	92	0.400
Jan. 26	9.8	460	1510	1430	5	290	10	80	95	0.450
Jan. 27	9.9	250	1380	1590	5	360	5	90	93	0.450
Jan. 28	10.0	350	1550	1540	10	330	10	150	90	0.450
Jan. 29	10.1	390	1750	1360	15	630	5	170	90	0.450
Jan. 30	10.0	370	1760	1800	10	420	10	175	90	0.450
Jan. 31	10.0	400	1540	1640	5	450	10	180	88	0.450
Feb. 1	10.0	380	1430	1540	10	570	5	170	88	0.450
Feb. 2	9.9	360	1570	1720	10	570	10	120	92	0.450
Feb. 3	9.9	380	1330	1810	10	280	10	100	92	0.450
Feb. 4	9.8	390	1440	1980	5	320	10	140	90	0.450
Feb. 5	9.6	430	1380	1840	10	260	10	160	88	0.450

Table XI-5 (Continued)

Date	Pretreated Feed			Effluent From Aeration Tank			Flocculated Effluent		TOD Removal	Flow Rate
	NaCl %	Glycols ppm	TOD ppm	MLVSS ppm	Glycols ppm	TOD ppm	Glycols ppm	TOD ppm	%	GPM
Feb. 6	9.9	500	1410	1930	15	290	20	190	86	0.450
Feb. 7	10.1	410	1610	1560	10	480	10	210	87	0.450
Feb. 8	9.7	460	1600	1180	10	380	10	140	91	0.450
Feb. 9	9.7	430	1340	1360	10	270	10	150	89	0.450
Feb. 10	9.5	425	1400	1660	10	270	10	80	94	0.450
Feb. 11	9.3	340	1280	1650	10	210	10	110	91	0.450
Feb. 12	9.1	370	1310	1430	10	240	10	160	88	0.450
Feb. 13	9.1	360	1020	1490	10	190	10	100	90	0.450
Feb. 14	9.1	340	1300	1710	10	230	10	140	89	0.450
Feb. 15	8.9	340	1300	1820	10	240	10	130	90	0.450
Feb. 16	8.9	360	1280	1680	10	270	10	150	88	0.450
Feb. 17	8.8	340	1260	2000	10	240	10	140	89	0.450
Feb. 18	8.7	290	1340	2020	10	180	10	150	89	0.450
Feb. 19	8.7	350	1400	1600	10	250	10	140	90	0.450
Feb. 20	8.7	420	1650	1660	10	270	10	180	89	0.450
Feb. 21	8.7	300	1680	1770	10	280	10	190	89	0.450
Feb. 22	8.7	270	1500	1550	10	270	10	130	91	0.450
Feb. 23	8.7	330	1240	1630	10	210	10	120	91	0.450
Feb. 24	8.8	380	1020	1540	10	140	10	100	90	0.450
Feb. 25	9.0	270	1140	1400	10	160	10	120	89	0.450
Feb. 26	8.9	360	1260	1380	10	180	10	120	91	0.450
Feb. 27	8.8	385	1170	1310	10	190	10	110	91	0.450
Feb. 28	8.7	330	1020	1520	10	190	10	100	90	0.450

Appendix C. Characteristics of Bacteria From the Activated Sludge Pilot Plant

Fresh activated sludge samples were plated out on nutrient agar containing both ethylene glycol and propylene glycol. The medium contained 6% NaCl and the dilutions were made at different concentrations up to 10% NaCl. One ml. samples were placed in sterile plastic petri-dishes, and were overlayed with 10 ml. of molten agar. The plates were incubated at room temperature (27°C). Each dilution was plated in triplicate. Forty-eight isolates were made from these samples and identified by number. Standard biochemical tests used in bacterial taxonomy were run on the pure cultures isolated from the activated sludge samples. These tests were (Bergey, 1957):

Oxidative-Fermentation Test of Hugh Liefson (O.F.)

Two tubes of medium containing glucose and acidity-alkalinity indicator are inoculated with a single bacterium. One tube is overlayed with sterile Squibb heavy duty mineral oil to effect anaerobic conditions. Growth in the tube only without mineral oil is read as "oxidative" and growth in the tube with mineral oil is read "fermentative". No indicator change is read as no change and is represented by a dash. This means that growth was not accompanied by production of either acid, or bases such as ammonia.

Lactose

Lactose fermentation is indicated by a + sign and no fermentation (i.e., acid or gas) is represented by a - sign. Each culture was inoculated into indicator broth containing a Durham tube and lactose. Acid was indicated by a change in color, and gas by accumulation of gas bubbles in the Durham tube immersed in the broth.

Oxidase Test

A drop of 4% aqueous dimethyl-p-phenylenediamine·HCl was applied to filter paper followed by a drop of the culture. A dark blue color is a positive oxidase test and is said to indicate the presence of cytochrome c. The test more or less correlates with the aerobic or facultative anaerobic state of oxidation.

Motility

Motility was determined using hanging drop slide and soft agar. In the latter case motile cells move beyond the site of the inoculation stab and result in turbidity extending beyond the stab. Motility is represented by a + sign.

Nitrogen Fixation

Growth in the absence of added nitrogen source is attributed to nitrogen fixation which occurs with certain bacteria. Nitrogen fixation is represented by a + sign.

Litmus Milk

Various reactions can take place in milk supplemented with the litmus indicator. Loss of color is reduction, blue color indicates base accumulation, red color indicates acid production and coagulation represents denaturation of protein. Acid production is represented by the letter A. and alkaline production is represented by the letter K.

NaCl

Growth on the indicated percent NaCl is indicated by a + sign.

Nitrate

Reduction of nitrate is indicated by a + sign. Nitrate reduction is exhibited by certain species of bacteria.

Catalase

Catalase is present in only certain species of bacteria. This enzyme is detected by addition of hydrogen peroxide to a colony on agar. Bubbles indicate the action of catalase.

Chitin

Growth on washed chitin (shrimp exoskeleton) indicates presence of chitinase. Very few bacteria synthesize chitinase.

Urea

Hydrolysis of urea to CO_2 and NH_3 by urease is exhibited by some bacteria and is an important diagnostic test. Urea hydrolysis is represented by a + sign.

Results and Discussion

The numbers of bacteria per ml. of sample, assuming one colony from one cell, were found to vary from a low of 2×10^6 to a high of 3.9×10^8. Results of the biochemical tests reactions for the Gram negative bacterial isolates are given in Table XI-6. Those for the few Gram positive isolates are given in Table XI-7. All of the bacteria, both

TABLE XI-6

BIOCHEMICAL TEST REACTIONS FOR GRAM NEGATIVE ROD BACTERIA FROM THE ACTIVATED SLUDGE

Culture Number	OF	Lactose	Oxidase	Motility	N_2 Fixation	Litmus Milk	0% NaCl	3% NaCl	6% NaCl
2	-	-	+	-	-	K	+	+	+
3	0	-	+	-	-	-	+	+	+
4	-	-	+	-	-	K	+	+	+
5	0	-	+	-	-	K	+	+	+
6	0	-	+	-	-	K	+	+	+
9	0	-	+	-	-	-	+	+	+
10	0	-	+	-	-	-	+	+	+
11a	-	-	+	-	-	K	+	+	+
13a	-	-	+	-	-	K	+	+	+
15	0	-	+	-	-	-	+	+	+
16a	0	-	+	-	-	K	+	+	+
19	0	-	+	-	-	K	+	+	+
20	-	-	+	-	-	K	+	+	+
21	-	-	+	-	-	K	+	+	+
22	-	-	+	-	-	K	+	+	+
24	-	-	+	-	-	K	+	+	+
28	0	-	+	-	-	-	+	+	+
36	0	-	+	-	-	K	+	+	+
37	0	-	+	-	-	-	+	+	+

Table XI-6 (Continued)

Culture Number	OF	Lactose	Oxidase	Motility	N_2 Fixation	Litmus Milk	0% NaCl	3% NaCl	5% NaCl
38	-	-	+	-	-	K	+	+	+
40	0	-	+	-	-	K	+	+	+
42	0	-	+	-	-	K	+	+	+
46	0	-	+	-	-	K	+	+	+
48	0	-	+	-	-	K	+	+	+
Serratia marcescens	F	+		+	-	A			
Pseudomonas fluorescens	-	-	+	-	-	-	+	+	+
Micrococcus luteus	0		-	-	-	-	+	+	+

TABLE XI-7

BIOCHEMICAL TEST REACTIONS FOR GRAM POSITIVE BACTERIA FROM THE ACTIVATED SLUDGE

Culture Number	Nitrate Reduction	Catalase	Lactose	Motility	Oxidase	OF	Chitin Hydrolysis	Urea	Litmus Milk
1	+	+	-	-	-	blue	+	+	-
11	+	+	-	-	-	blue	+	+	-
13	+	+	-	-	-	blue	+	+	-
16	+	+	-	-	-	blue	+	+	-
19	+	+	-	-	-	blue	+	-	-
39	+	+	-	-	-	blue	+	+	-

the Gram positive and the Gram negative rods are negative for lactose fermentation, motility, and the Hugh-Liefson fermentation test.

It was concluded from the biochemical test reactions and from colony appearance that there are no more than 2 to 4 different bacteria in these isolates from the brine activated sludge. There were a few filamentous fungal spores and a few colonies were obtained on plating of the liquids. The Gram positive bacterium is not prevalent. The most numerous bacterium is a Gram negative, non-motile, lactose negative, oxidase positive, rod. It is not the same as Bacterium T-52 isolated from the Great Salt Lake, because Bacterium T-52 is oxidase negative.

Appendix D. Design Calculations and Cost Estimates of a 6 MGD Activated Sludge Plant

The details of the design calculations, equipment specifications and the installed cost of each item of equipment installed including the piping are presented in this section, grouped under the pretreatment, aeration and settling, sludge handling and general services sections.

I. Pretreatment and Cooling

The pretreatment of the glycol wastewater includes neutralization, cooling and equalization, nutrient addition, and dilution water addition.

Neutralization

Feed rate $= 6 \times 10^{6} \times \frac{\text{gal.}}{\text{day}} \times 1.063 \times 8.34 \frac{\text{lbs.}}{\text{gal.}}$

$= 53.2 \times 10^{6}$ lbs./day

Anhydrous HCl requirement $= 53.2 \times 10^{6} \times \frac{0.18}{100} \times \frac{36.5}{40} \times 0.9$

$= 78{,}750$ lbs./day

$= 2.87 \times 10^{7}$ lbs./year

38% HCl requirement $= 78{,}750 \times \frac{100}{38} \times \frac{1}{9.92} \frac{\text{gals.}}{\text{lb.}}$

$= 21{,}000$ gallons /day $= 14.5$ gpm

Cost of HCl at 0.015 \$/Lb. $= 2.87 \times 10^{7} \times 0.015$

$= 431{,}000$ \$/yr.

D-1 Surge Tank for 38% Hydrochloric Acid

Specifications:		
	Volume	30,000 gallons
	Dimensions	18 ft. diameter x 18 ft. high
	Lining	rubber

Intalled Cost Breakdown:

Item	Quantity	Units	Cost Distribution ($) Labor	Material	Rental	Total
30,000 gal. rubber lined tank	1	each	2,000	13,000	-	
Foundation	8	cu.yd.	120	160	40	
Site preparation & leveling	400	sq.ft.	40		40	
Painting	1500	sq.ft.	600	600		
Piping & fittings	100	ft.	300	300	—	
Total Rentals					80	$ 80
Total Materials				14,060		14,060
Total Labor			3,060			3,060
Contractor's Allowance						
35% of Labor				1,070		
18% of Materials				2,540		
105% of Rentals				90		
Total Allowance				3,700		$ 3,700
JOB COST						$20,820
Engineering, 15%						3,130
Contingencies, 15%						3,130
TOTAL INSTALLED COST						$27,100

P-1A, P-1B Hydrochloric Acid Pumps

Specifications:	Each of two pumps to deliver 16 gpm. of 38% HCl at 30 psi. Goulds Model 3107 Teflon lined, 1 x 1 x 6, driven at 3600 rpm. by 5 H.P. Class I, Group D electric motor. Pump equipped with John Crane mechanical seal (8 x P1CH) or equivalent.

Installed Cost Breakdown:

Item	Quantity	Units	Cost Distribution ($)			Total
			Labor	Material	Rental	
Pump & motor	2	each	592	2,040	-	
Foundation	2	cu.yd	40	40		
Electrical	10	KVA	250	250		
Painting	50	sq.ft.	20	20		
Piping & fittings	100	ft.	300	300		
Total Materials				2,650		$ 2,650
Total Labor			1,202			1,202
Contractor's Allowance						
35% of Labor				420		
18% of Materials				480		
Total Allowance				900		900
JOB COST						$ 4,752
Engineering, 15%						714
Contingencies, 15%						714
TOTAL INSTALLED COST						$ 6,180

Cooling and Equalization

The base of design of a cooling and equalization pond are chosen for operating conditions during the summer months.

Wastewater flow, F = 4,200 gal./min.
Inlet temperature, T_1 = 180 °F
Outlet temperature, T_2 = 105 °F
Dry-bulb air temperature (3 day max. avg.) = 85 °F
Relative humidity, R.H. = 50 %
Wind velocity, V_W (daily avg.) = 8 m.p.h.
Solar heat gain, Q_S (24 hr. avg.) = 130 BTU/hr./sq.ft.
Hold-up time = 2 days

The cooling pond surface area is determined from Nomographs, found on pages 15-22 and 15-23 of Perry's Chemical Engineering Handbook, 4th Edition.

The P factor found is 84 and the Q factor is 0.75.

Surface area = F x PQ = 4200 x 0.75 x 84
= 263,600 sq. ft.
Volume = 2 x 6 = 10^6 = 12 x 10^6 gallons
= 1.6 x 10^6 cu. ft.

The cooling pond and the aeration basin share a common wall, through which a 3 ft. x 3 ft. Parshall flume is installed to conduct the feed to the aeration basin. The slope of the levees is 2 ft. horizontally to 1 ft. vertical rise, which provides long-term stability with minimum erosion due to storm water run-off. The two basins are designed such that the excavated depth generates the dirt required for the above-grade earthen levees. A computer program was used for these calculations.

EC-1 Equalization and Cooling Pond

Specifications:	Surface area	264,800 sq. ft.
	Bottom width & length	489 ft.
	Top inside width & length	519 ft.
	Total depth of pond	7.35 ft.
	Levee height above grade	6.7 ft.
	Film (0.03 in. thick), covered surface area	272,460 sq. ft.

Installed Cost Breakdown:

Item	Quantity	Units	Cost Distribution ($) Labor	Material	Rental	Total
Excavation	5528	cu.yd.	2210		1550	
Spreading & compacting	12,735	cu.yd.	2100		3560	
Film lining of bottom & sides	272,455	sq.ft.	65,400	43,600		
Concrete for Parshall Flume	40	cu.yd	800	1,000	200	
Total Rentals					5310	$ 5,310
Total Materials				44,600		44,600
Total Labor			73510			73,510
Contractor's Allowance						
35% of Labor				25,700		
18% of Materials				8,030		
105% of Rentals				5,580		
Total Allowance				39,310		39,310
JOB COST						$162,730
Engineering, 15%						24,410
Contingencies, 15%						24,410
TOTAL INSTALLED COST						$211,550

Nutrient Addition

Ammonia and phosphoric acid are added to the aeration basin to supply the nitrogen and phosphorus at a concentration of each in proportion to the TOD removed.

TOD removed

$$= 53.2 \times 10^6 \left(\frac{\text{lbs.}}{\text{day}}\right) \times (1400-140) \times 10^{-6}$$

$$= 67{,}000 \text{ lbs./day}$$

Anhydrous ammonia requirement

$$= \frac{67{,}000}{30} \times \frac{17}{14}$$

$$= 2720 \text{ lbs./day}$$

$$= 2720 \times \frac{1}{5.16} = 527 \text{ gallons/day}$$

$$= 0.366 \text{ gpm.}$$

Cost of ammonia

$$= 2720 \frac{\text{lbs.}}{\text{day}} \times 365 \frac{\text{days}}{\text{year}} \times 0.032 \frac{\$}{\text{lb.}}$$

$$= 30{,}900 \text{ \$/year}$$

Phosphoric acid (75% H_3PO_4) requirement

$$= \frac{67{,}000}{300} \times \frac{98}{31} \times \frac{100}{75}$$

$$= 950 \text{ lbs./day}$$

$$= 950 \times \frac{1}{13.1} = 72.4 \text{ gallons/day}$$

$$= 0.05 \text{ gpm.}$$

Cost of phosphoric acid

$$= 950 \frac{\text{lbs.}}{\text{day}} \times 365 \frac{\text{days}}{\text{yr.}} \times 0.0695 \frac{\$}{\text{lb.}}$$

$$= 24{,}100 \text{ \$/year}$$

D-2 Ammonia Storage Tank

Specifications:		
	Volume	10,000 gallons
	Pressure vessel designed for 600 psi.	
	Dimensions	8 ft. diameter x 24 ft. long horizontal tank
	Material	carbon steel

Installed Cost Breakdown:

Item	Quantity	Units	Cost Distribution ($) Labor	Material	Rental	Total
Pressure vessel	1	each	2800	14,000	-	
Foundation	60	cu.yd.	900	1,200	300	
Insulation	800	sq.ft.	2000	2,000		
Paint	800	sq.ft.	320	320		
Piping & fittings	100	ft.	800	800		
Total Rentals					300	$ 300
Total Materials				18,320		18,320
Total Labor			6820			6,820
Contractor's Allowance						
35% Labor				2,400		
18% Materials				3,300		
105% Rentals				320		
Total Allowance				6,020		6,020
JOB COST						$31,160
Engineering, 15%						4,670
Contingencies, 15%						4,670
TOTAL INSTALLED COST						$40,500

D-4 Phosphoric Acid Storage Tank

Specifications:		
	Volume	7,500 gallons
	Dimensions	11 ft. diameter x 11 ft. high
	Material	316 stainless steel

Installed Cost Breakdown:

			Cost Distribution ($)			
Item	Quantity	Units	Labor	Material	Rental	Total
Vessel	1	each	2500	11,000		
Leveling & site preparation	200	sq.ft.	20	20		
Concrete	2	cu.yd.	40	60	10	
Painting	600	sq.ft.	240	240		
Piping & fittings	100	ft.	400	400	—	
Total Rentals					10	$ 10
Total Materials				11,720		11,720
Total Labor			3200			3,200
Contractor's Allowance						
35% of Labor				1,120		
18% of Materials				2,110		
105% of Rentals				10		
Total Allowance				3,240		3,240
JOB COST						$18,160
Engineering, 15%						2,720
Contingencies, 15%						2,720
TOTAL INSTALLED COST						$23,600

P-4A and P-4B Phosphoric Acid Pumps

Specifications:	Each of two pumps circulating 75% H_3PO_4 at a rate of 5 gpm. over a constant head device (60 ft. head). A feed rate of 0.05 gpm. from this loop is controlled by a signal from a flow recorder controller (FRC-4). Goulds Model 2520, 316 stainless steel self-priming centrifugal pumps with 5 H.P., 1750 rpm. motor, Faulk coupling and Crane 9TQP1C1 mechanical seal or equivalent.

Installed Cost Breakdown:

Item	Quantity	Units	Cost Distribution ($)			Total
			Labor	Material	Rental	
Pump & motor	2	each	440	1,530		
Foundation	2	cu.yd.	90	90		
Electrical	10	KVA	250	250		
Painting	100	sq.ft.	40	40		
Piping & fittings (SS)	150	ft.	450	900		
Total Materials				2,810		$ 2,810
Total Labor			1,270			1,270
Contractor's Allowance						
35% of Labor				445		
18% of Material				506		
Total Allowance				951		951
JOB COST						$ 5,031
Engineering, 15%						755
Contingencies, 15%						754
TOTAL INSTALLED COST						$ 6,540

Dilution Water

Dilution water is added to replace the water lost by evaporation in the cooling pond in order to maintain the salt content at 9% and to supply the trace minerals required for bacterial growth.

Assuming 1000 BTU/lb. of water vaporized to cool the waste-water from 180°F. to 100°F., then:

Heat loss $= 53.2 \times 10^{6} \left(\frac{\text{lbs.}}{\text{day}}\right) \times (180-100)\ (^\circ\text{F.})$

$\times\ 1.0\ \frac{\text{BTU}}{\text{lb. }^\circ\text{F.}}$

$= 4.256 \times 10^{9}$ BTU/day

Water lost by evaporation $= \frac{4.256 \times 10^{9}}{1000} = 4.256 \times 10^{6}$ lbs./day

$= 2,960$ lbs./min.

River water requirement $= 2960$ lbs./min.

$= 355$ gpm.

Seawater (2.5% salt) requirement is calculated from a salt balance:

$$\frac{36,900 \times 0.09 + W \times 0.025}{(36,900-2,960) + W} = 0.09$$

therefore:

$$W = 4100 \text{ lbs./min} = 480 \text{ gpm.}$$

P-6A and P-6B Dilution Water Pumps

Specifications:	Each of two pumps to deliver 800 gpm. at 26 psi. Goulds Model 3196, 4 in. x 6 in. x 12.75 in. (CDS 1784), driven at 1150 rpm by 20 H.P. electric motors.

Installed Cost Breakdown:

			Cost Distribution ($)			
Item	Quantity	Units	Labor	Material	Rental	Total
Pump & motor	2	each	1,000	2,600		
Foundation	2	cu.yd.	50	50		
Electrical	40	KVA	800	800		
Painting	150	sq.ft.	60	60		
Piping & fittings (8 in. pipe)	50	ft.	400	400		
Total Materials				3,910		$ 3,910
Total Labor			2,310			2,310
Contractor's Allowance						
35% of Labor				810		
18% of Materials				705		
Total Allowance				1515		1,515
JOB COST						$ 7,735
Engineering, 15%						1,163
Contingencies, 15%						1,162
TOTAL INSTALLED COST						$10,060

II. Aeration and Settling

The neutralized and cooled wastewater is fed to the aeration basin through a Parshall flume from the cooling pond. The nutrients and dilution water are mixed in the aeration basin. The overflow from the aeration to a clarifier is separated into settled sludge and treated effluent.

Aeration Basin

The aeration basin is designed to remove 90% of the TOD in the feed and produce an effluent of average TOD concentration of 140 ppm.

Feed rate = 4200 gpm.

TOD_f = 1400 ppm.

TOD_e = 140 ppm.

Recycle ratio = 25 %

$$TOD_i = \frac{1400 + 0.25\ (140)}{1.25} = 1150 \text{ ppm.}$$

For a mixed liquor volatile suspended solids (MLVSS) of 1500 ppm:

$$\frac{TOD_i - TOD_e}{t_i \times TOD_e} = 1.33 - 0.412 \left(\frac{TOD_i}{MLVSS}\right), \text{ (Figure VII-16)}$$

$$\frac{1150 - 140}{t_i\ (140)} = 1.33 - 0.412 \left(\frac{1150}{1500}\right)$$

therefore:

t_i = 7.1 hours

t_f = 8.86 hours, based on feed rate.

Volume of basin = 4200 x 60 x 8.86 = 2,300,000 gallons
= 300,000 cu. ft.

Weight TOD removed $= 53.2 \times 10^6 \times \frac{1400-140}{10^6} = 67{,}200$ lbs./day

Weight of Mixed liquor in basin $= 2.3 \times 10^6 \times 8.87$

$= 19.7 \times 10^6$ lbs.

Weight of MLVSS in basin $= 19.7 \times 10^6 \times 1500 \times 10^{-6}$

$= 29{,}500$ lbs.

Loading $= \frac{67{,}200}{29{,}500} = 2.28$ lbs. TOD removed/lb. MLVSS·day

Oxygen Requirement

Lbs. oxygen consumed per day = 0.256 (lbs. TOD removed/day) + 0.13 (lb. MLVSS)

= 21,000 lbs./day

$$N_o = \frac{N}{\left(\frac{C_{SW} - C_L}{C_{SH_2O}}\right) (1.028)^{t-20} (\alpha)}$$

where:

N = lbs. oxygen consumed per day = 21000 lbs./day

N_o = lbs. oxygen transferred per day to clear water at 20°C.

C_{SW} = saturation value of oxygen in the waste at temperature t. (3.5 ppm.)

C_L = operating dissolved oxygen level (1.0 ppm.)

C_{SH_2O} = saturation value of oxygen in tap water at 20°C. (9.2 ppm.)

α = oxygen transfer coefficient for the treated wastewater = 1.2

t = temperature of the aeration basin = 85°F. = 29.4°C.

$$N_o = \frac{9.2 \times 21{,}000}{(3.5-1.0)(1.028)^{9.4}(1.2)}$$

$= 49{,}700$ lbs. O_2/day

$= 2{,}070$ lbs. O_2/hr.

Brake H.P. required $= \frac{2{,}070}{3.2} = 648$ H.P.

Surface aerators, (9 x 75 H.P.), rated at 3.2 lbs. of oxygen transfer per hour per brake horse power are required.

A-6 Aeration Basin

Specifications:		
	Volume	300,000 cu. ft.
	Bottom width & length	129 ft.
	Top inside width & length	189 ft.
	Total depth	15 ft.
	Levee height above grade	6.7 ft.
	Water depth	12.5 ft.
	Freeboard above water level	2.5 ft.

Installed Cost Breakdown:

			Cost Distribution ($)			
Item	Quantity	Units	Labor	Material	Rental	Total
Excavation	6,567	cu.yd.	2,630		1,840	
Spreading & compacting	5,263	cu.yd.	2,100		1,470	
Film lining of bottom & sides	38,069	sq.ft.	9,150	6,100		
Concrete base under aerators	67	cu.yd.	1,000	1,350	350	
Floating surface aerators	9	each	4,500	67,500		
Mooring cables & anchores	9	each	450	540		
Electrical	600	KVA	15,000	15,000		
Painting	2,000	sq.ft.	800	800		
Piping (18 in. underground)	100	ft.	1,500	1,500		
Total Rentals					3,660	$ 3,660
Total Materials				92,790		92,790
Total Labor			37,130			37,130
Contractor's Allowance						
35% of Labor				13,000		
18% of Material				16,700		
105% of Rentals				5,100		
				34,800		34,800
JOB COST						$164,720

A-6 Aeration Basin (Continued)

Engineering, 15%	24,600
Contingencies, 15%	24,600
TOTAL INSTALLED COST	$214,000

Clarifier

The data presented in Figure VII-24 is used to design the clarifier.

$$\text{Overflow rate, (O.R.)} = \frac{d \times 7.48 \times 1440}{t} \text{ gal./day/ft.}^2$$

where

d = depth of the experimental column = 6 ft.

t = settling time in minutes.

Using the method described by Ekenfelder (1962), the following table can be calculated from the data of Figure VII-24.

Time (min.)	Velocity ft./hr.	Removal %	O.R. gal./ft.^{2}/day
10	36	49	6,500
15	24	75	4,300
21	17	90	3,000

For 90% removal,

O.R. = 3,000 gpd/ft.^{2}

t = 21 minutes

Using a scale-up factor of 2.0,

O.R. = 1,500 gpd/ft.^{2}

t = 42 minutes

For a Dorr-Oliver Clarifier, 75 ft. diameter and 6 ft. deep,

surface area = 4,400 sq. ft.

$$\text{O.R.} = \frac{6 \times 10^6}{4400} = 1370 \text{ gpd/ft.}^2$$

volume = 26,400 cu. ft. = 197,500 gallons

$$\text{retention time, } t = \frac{197{,}500 \times 60}{6 \times 10^6} = 47 \text{ minutes}$$

CL-7 Clarifier

Specifications: Concrete base, steel tank with raking arms and sludge vacuum pick-up. (Dorr-Oliver or equivalent).

Diameter = 75 ft.
Depth = 6 ft.

Installed Cost Breakdown:

Item	Quantity	Units	Cost Distribution ($)			Total
			Labor	Material	Rental	
Excavation	800	cu.yd.	320		224	
Reinforced concrete	100	cu.yd.	1,500	2,000	500	
Clarifier, tank, rakes, etc.	1	each	29,000	112,500		
Electrical	5	KVA	350	350		
Piping & fittings	140	ft.	1,660	1,660		
Painting	2,000	sq.ft.	800	800		
Total Rentals					724	724
Total Materials				117,310		$117,310
Total Labor			33,630			33,630
Contractor's Allowance						
35% of Labor				11,760		
18% of Materials				21,100		
105% of Rentals				760		
Total Allowance				33,640		33,640
JOB COST						$184,580
Engineering, 15%						27,700
Contingencies, 15%						27,700
TOTAL INSTALLED COST						$239,980

P-7A and P-7B Sludge Recycle Pumps

Specifications:	Each of two pumps to deliver up to 2400 gpm. of sludge at 15 psi. Goulds Model 3175 (CDS 1998) or equivalent, 8 in. x 10 in.-18 in. powered by 40 H.P., 880 rpm. electric motors.

Installed Cost Breakdown:

			Cost Distribution ($)			
Item	Quantity	Units	Labor	Material	Rental	Total
Pumps & motors	2	each	2,000	6,450		
Foundation	2	cu.yd.	50	50		
Electrical	80	KVA	1,600	1,600		
Painting	100	sq.ft.	40	40		
Piping & fittings	50	ft.	800	800		
Total Materials				8,940		$ 8,940
Total Labor			4,490			4,490
Contractor's Allowance						
35% of Labor				1,570		
18% of Materials				1,610		
Total Allowance				3,180		3,180
JOB COST						$16,610
Engineering, 15%						2,490
Contingencies, 15%						2,500
TOTAL INSTALLED COST						$21,600

Sludge Recycle

The sludge blanket in the clarifier is calculated to be about 1.25 feet deep. The concentration of MLVSS in the sludge return averages about 7000 ppm. The flow of 25% recycle is 1050 gpm., and is pumped from the clarifier to the aeration basin.

III. Sludge Handling

The excess sludge formed is calculated using data shown in Figure VII-22.

Lbs. VSS formed/day = 0.133 (lbs. TOD removed/day) - 0.04 (MLVSS)

therefore:

Excess sludge = 0.133 (67,000) - 0.04 (29,500)
= 7730 lbs./day
= 5.37 lbs./minute

This excess sludge is removed in a stream from the sludge recycle, having the same concentration of about 7000 ppm. of volatile suspended solids. This flow of 92 gpm. is thickened to a 3.2% solids and centrifuged to 18% solids, then hauled to landfill.

Sludge Thickener

The sludge was found to compact to a 3.2% solids. A sludge thickener for this sludge is designed for an overflow rate of 400 gals./day/ft.^{2} and a residence time of 2 hours.

Underflow from thickener = 20.2 gpm., (3.2% solids)

Overflow from thickener = 92 - 20.2 = 71.8 gpm.

Surface area $= \frac{71.8 \times 1440}{400} = 259$ sq. ft.

Volume = 2 x 60 x 92 = 11,040 gallons
= 1474 cu. ft.

Depth $= \frac{1474}{259} \simeq 6$ ft.

Diameter = 18 ft.

Centrifuging

Limited laboratory experiments showed the sludge to centrifuge to 18% to 20% solids, easier than filtration.

The overflow from the centrifuges will be 16.6 gpm. while the sludge discharged at 18% solids will be about 3.6 gpm.

IV. General Services

Included under general services are the piping not included in equipment installation costs, buildings for office, laboratory and instrument room, control instruments and roads and parking lots.

THK-8 Sludge Thickener

Specifications:
Diameter = 18 ft.
Surface area = 254 ft.^{2}
Depth = 6 ft.
Overflow rate = 400 gpd/ft.^{2}
A Dorr-Oliver settling tank with mechanical raking arms.

Installed Cost Breakdown:

			Cost Distribution ($)			
Item	Quantity	Units	Labor	Material	Rental	Total
Tank & rakes	1	each	5,300	27,000		
Concrete	6	cu.yd.	150	150		
Electrical	10	KVA	250	250		
Painting	1500	sq.ft.	600	600		
Piping & fittings	240	ft.	660	700		
Total Materials				28,700		$28,700
Total Labor			7,060			7,060
Contractor's Allowance						
35% of Labor				2,470		
18% of Materials				5,170		
Total Allowance				7,640		7,640
JOB COST						$43,400
Engineering, 15%						6,500
Contingencies, 15%						6,500
TOTAL INSTALLED COST						$56,400

CF-9AXB Centrifuges

Specifications:	Each of two centrifuges of 20-40 gpm. capacity driven by a 25 H.P. motor at an operating speed of 3000 to 6000 rpm. Dorr-Oliver Model 12-L or equivalent.

Installed Cost Breakdown:

Item	Quantity	Units	Cost Distribution ($)			Total
			Labor	Material	Rental	
Centrifuge	2	each	7,000	70,000		
Electrical	60	KVA	1,500	1,500		
Foundations	30	cu.yd.	600	600		
Painting	1000	sq.ft.	400	400		
Piping & fittings	2	each	4,000	4,000		
Total Materials				76,500		$ 76,500
Total Labor			13,500			13,500
Contractor's Allowance						
35% of Labor				4,800		
18% of Materials				13,700		
Total Allowance				18,500		18,500
JOB COST						$108,500
Engineering, 15%						16,250
Contingencies, 15%						16,250
TOTAL INSTALLED COST						$141,000

P-8A and P-8B Sludge Pumps Forwarding From Thickener To Centrifuges

Specifications: Each of two pumps delivering 20-40 gpm. of sludge (3.2% solids) at 40 psi.
Goulds or equivalent, Model 3196, 1 x 1-1/2 x 8 powered by 5 H.P. motor at 1750 rpm.

Installed Cost Breakdown:

Item	Quantity	Units	Cost Distribution ($)			Total
			Labor	Material	Rental	
Pump & motor	2	each	400	1,070		
Foundation	2	cu.yd.	50	50		
Electrical	10	KVA	250	250		
Painting	100	sq.ft.	40	40		
Total Materials				1,410		$ 1,410
Total Labor			740			740
Contractor's Allowance						
35% of Labor				260		
18% of Materials				250		
Total Allowance				510		510
JOB COST						$ 2,660
Engineering, 15%						400
Centingencies, 15%						400
TOTAL INSTALLED COST						$ 3,460

P-9A and P-9B Pumps for Overflow From Thickener and Centrifuges

Specifications: Each of two pumps to deliver 160 gpm. at 73 psi.
Goulds Model 3196, 316 S.S., 2 x 3 -8 (6-1/2 in.) driven by 20 H.P. 3500 rpm. electric motor.

Installed Cost Breakdown:

			Cost Distribution ($)			
Item	Quantity	Units	Labor	Material	Rental	Total
Pump & motor	2	each	1,030	2,450		
Foundation	2	cu.yd.	50	50		
Painting	75	sq.ft.	30	30		
Electrical	40	KVA	1,000	1,000		
Piping & fittings	50	ft.	250	250		
Total Materials				3,780		$ 3,780
Total Labor			2,360			2,360
Contractor's Allowance						
35% of Labor				826		
18% of Materials				681		
Total Allowance				1,507		1,507
JOB COST						$ 7,647
Engineering, 15%						1,142
Contingencies, 15%						1,141
TOTAL INSTALLED COST						$ 9,930

Piping Not Included With Equipment

Installed Cost Breakdown:

			Cost Distribution ($)			
Item	Quantity	Units	Labor	Material	Rental	Total
14 in. pipe to cooling pond includes one overhead road crossing and one valve.	20	ft.	3,360	3,360		
14 in. pipe recycling sludge from clarifier to aerator.	400	ft.	7,200	7,200		
8 in. pipe for dilution water	160	ft.	3,330	3,330		
Total Materials				13,890		$13,890
Total Labor			13,890			13,890
Contractor's Allowance						
35% of Labor				3,500		
18% of Materials				2,500		
Total Allowance				6,000		6,000
JOB COST						$33,780
Engineering, 15%						5,100
Contingencies, 15%						5,100
TOTAL INSTALLED COST						$43,980

Control Instruments

Specifications: As in instrument list

Installed Cost Breakdown:

Item	Quantity	Units	Cost Distribution ($)			Total
			Labor	Material	Rental	
Total Base Cost	1	all	8,500	16,820		
Piping			2,000	5,180		
Instrument Panel	1	each	250	500		
Structural			250	500		
Electrical			800	1,700		
Painting			200	100		
Total Materials				24,800		$24,800
Total Labor			12,000			12,000
Contractor's Allowance						
35% of Labor				4,400		
18% of Materials				4,600		
Total Allowance				9,000		9,000
JOB COST						$45,800
Engineering, 15%						6,900
Contingencies, 15%						6,900
TOTAL INSTALLED COST						$59,600

Instrument List and Cost Estimate

Tag Item	Description	Cost, $
LT - 1	Foxboro M13FA-HS teflon-faced, WM-13R-HS-315 repeater	970
L1C - 1	Foxboro M43A-A2-PC3-15	270
LV - 1	Annin 1560 with Kynar body and trim	445
LI - 1	Moore receiver gauge	19
pHT - 1	Foxboro M699A-FN pH converter electrodes and holder	965
pHRC - 1	Foxboro M5422-Ts, with M58P4 controller	865
pHV - 1	Annin 1560 with Kynar body and trim, 1 in. CV = 10	445
FO - 1	14 in. slip-on meter run flanges	740
FE - 1	14 in. hastelloy "C" orifice plate	350
FT - 1	Foxboro M13A - MS-2	287
FR - 1	Second pen of pHRC-1	
FI - 1	Moore receiver gauge	19
PI - 1	Ashcroft M-1279-S	32
PI - 2	Ashcroft M-1279-S	32
LT - 2	Foxboro 13A-HS-2R	297
LIC - 2	Foxboro M43A-A2-PG315	270
LV - 2	Annin 1560 SS 316 1 in.	283
FT - 2	Foxboro M13A-MS2	287
FO - 2	I/O manifold, 316 SS orifice	97
FRC - 2	Foxboro M5422-Ts with M58P4 controller	865
PT - 2	Foxboro M-11GM-AS-2	296
PR - 2	Second pen of FRC-2	
PSV - 2	Crosby 2-1/2 J4 style J035 or equal	700
FV - 2	Annin 1560 1 in - 150 lb. flanged, SS	342
LT - 4	Foxboro M13A-MS2	287
LI - 4	Moore receiver gauge	19
FT - 4	Foxboro M13A-MS-2	287
FO - 4	I/O manifold, 316 SS orifice	97

Instrument List and Cost Estimate (Continued)

Tag Item	Description	Cost, $
FRC - 4	Foxboro M5422TS with M58P4 controller	865
FV - 4	Annin 1560, 1 in. - 150 lb. flanged 316 SS	342
AT - 5	Dynatrol S.G. (1.0 to 1.1) $3200 OR	
	Foxboro M15A D/P cell with stand pipe assembly	600
ARC - 5	Foxboro M5422-TS and M58P-4	865
AV - 5	Annin - Butterfly, 3 in. flanged	680
FT - 5	Foxboro M13A-MS2	287
FE - 5&6	Parshall flumes, 3 ft. x 3 ft.	1,000
pHT - 6	Foxboro M699A-FN complete	965
pHR - 6	Second pen of ARC - 5	
TR - 1	Bristol 12PG570 includes $400 for thermocouples	1,692
TR - 2	one point on above	
TOTAL COST		$16,862

Instrument Air Supply

Specifications:

Capacity 29 CFM
Pressure 125 psig.
Unitized with dryer and 120 gallon receiver tank and cooler.
Ingersol-Rand Model 57-T or equivalent.

Installed Cost Breakdown:

Item	Quantity	Units	Cost Distribution ($) Labor	Material	Rental	Total
Compressors	2	each	200	6,000		
Piping, 1 in.	100	ft.	150	150		
Reinforced concrete	2	cu.yd.	50	50		
Electrical	20	KVA	400	400		
Painting	100	sq.ft.	40	40		
Total Materials				6,640		$ 6,640
Total Labor			840			840
Contractor's Allowance						
35% of Labor				310		
18% of Material				1,210		
Total Allowance				1,520		1,520
JOB COST						$ 9,000
Engineering, 15%						1,350
Contingencies, 15%						1,350
TOTAL INSTALLED COST						$11,700

Office and Laboratory Building

Specifications: 40 ft. x 60 ft. air-conditioned building

Installed Cost Breakdown:

			Cost Distribution ($)			
Item	Quantity	Units	Labor	Material	Rental	Total
Shell	2,400	sq.ft.	7,200	12,000		
Heating & cooling	2,400	sq.ft.	7,200	9,600		
Lighting	2,400	sq.ft.	3,600	2,400		
Plumbing	2,400	sq.ft	2,400	2,400		
Laboratory Equipment	400	sq.ft.	3,200	8,000		
Office Equipment	400	sq.ft.	400	2,000		
Shop Equipment	400	sq.ft.	400	2,000		
Fire Protection	2,400	sq.ft	2,400	2,400		
Total Materials				40,800		$ 40,800
Total Labor			26,800			26,800
Contractor's Allowance						
35% of Labor				9,300		
18% of Materials				7,400		
Total Allowance				16,700		16,700
JOB COST						$ 84,300
Engineering, 15%						12,300
Contingencies, 15%						12,400
TOTAL INSTALLED COST						$109,000

Roads and Parking Lots

Specifications: 22 ft. wide; 2 in. asphalt over 1 ft. of sand stabilized shell or equivalent.

Installed Cost Breakdown:

Item	Quantity	Units	Cost Distribution ($) Labor	 Material	 Rental	Total
Roadway & parking lot	25,000	sq.ft.	10,000	12,500	2,500	
Total Rentals					2,500	$ 2,500
Total Materials				12,500		12,500
Total Labor			10,000			10,000
Contractor's Allowance						
35% of Labor				3,500		
18% of Materials				2,250		
105% of Rentals				2,750		
Total Allowance				8,500		8,500
JOB COST						$31,000
Engineering, 15%						4,650
Contingencies, 15%						4,650
TOTAL INSTALLED COST						$40,300

Appendix E. Microbial Metabolism of Ethylene and Propylene Glycols in Presence of Sodium Chloride

by

Dr. Willard A. Taber, Department of Biology
Texas A. & M. University, College Station, Texas

ABSTRACT

Many bacteria, fungi and algae were tested for capacity to metabolize ethylene glycol and propylene glycol in the presence of high concentrations of sodium chloride. The algae did not grow well in the presence of salt and only a small percent of the bacteria and fungi utilized either ethylene glycol or propylene glycol. A still smaller percent could utilize both glycols. A fungus (Fusarium) referred to as Fungus T-83 was isolated which was capable of growing on ethylene glycol in diluted waste water and respiring on neutralized but undiluted waste water enriched with ethylene glycol. A bacterium (Acinetobacter) referred to as Bacterium T-52 was isolated from a solar evaporation pond, Great Salt Lake, Utah, which could grow on both ethylene glycol and propylene glycol in synthetic media containing 12% NaCl and glycol, and in undiluted but neutralized waste water containing glycol. Diagnostic and nutritional characteristics of the bacterium are given. It is a Gram negative, non-motile, oxidase negative, non-fermentative rod which cannot grow on lactose or cetrimide, produce indole or hydrolyze urea. It can reduce nitrate. It does not require an external source of vitamins for growth but does require sodium ion, which cannot be replaced by potassium ion. Approximately 1 gram/liter medium NaCl is required. Maximal growth occurs between 3.4% and 7% NaCl but growth is fairly abundant in the presence of 12% NaCl. It will not grow well below pH 5.4. It is killed by high concentrations of dichloroethylether and ethylene chlorohydrin but not by ethylene dichloride. Studies with radioactive ethylene glycol and propylene glycol revealed that this bacterium can readily assimilate and respire both of these glycols. When the culture is grown on radioactive glycol in the presence of suboptimal amount of nitrogen source, the culture converts most of the glycol carbon to carbon dioxide carbon. The presence of glucose suppresses glycol metabolism but does not completely prevent it.

The detailed report is available on request from Dr. Willard A. Taber of the Department of Biology, Texas A. & M. University, College Station, Texas 77840.

1 Accession Number	2 Subject Field & Group Ø5G	**SELECTED WATER RESOURCES ABSTRACTS** **INPUT TRANSACTION FORM**

5 Organization

The Dow Chemical Company
Texas Division
Freeport, Texas 77541

6 Title

Treatment of Wastewater From The Production of Polyhydric Organics

10 Author(s) M. A. Zeitoun W. F. McIlhenny	16 Project Designation EPA, Project No. 12020-EEQ 21 Note

22 Citation

23 Descriptors (Starred First)

Brine Wastewaters*, Wastewaters From Glycol Production*, Biological Treatment*, Renovation Methods*, Solvent Extraction, Carbon Adsorption, Membrane Separations, Activated Sludge

25 Identifiers (Starred First)

Wastewater Characterization*, Treatability*, Pilot Plant Operation*. Plug Flow and Completely mixed activated sludge. Design of Activated Sludge From Pilot Plant Data. Cost Estimate.

27 Abstract

The brine wastewater resulting from the production of glycols, by the chlorohydrin process, is characterized by high salt content (8-10% NaCl) excess alkalinity, and the presence of several organic compounds.

Solvent extraction of the glycol wastewater with amines produces a raffinate that is salt-saturated and a product enriched in glycol. The required large solvent-to-feed ratio and operation at near freezing temperatures make the process uneconomical. Adsorption of glycols on activated carbon was found unfeasible because of the low capacity of carbon for the glycols. Cellulose acetate membranes with low salt rejection were unable to significantly separate the salt and glycol.

Activated sludge pilot plant was successfully operated for the treatment of an equalized glycol wastewater. Removal of over 90% of the TOD at a retention time of 8.0 hours and loadings of 2.0 to 3.0 lbs. TOD/lb. MLVSS·day were obtained. Design parameters determined from pilot plant operation were used to design a 6 MGD treatment plant, at an estimated cost of 3.3 cents per pound of TOD removed or less than 0.2 cents per pound of propylene glycol produced.

Abstractor M. A. Zeitoun	Institution The Dow Chemical Company

WR:102 (REV. JULY 1969)
WRSIC

SEND TO: WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U.S. DEPARTMENT OF THE INTERIOR
WASHINGTON, D. C. 20240

☆U.S. GOVERNMENT PRINTING OFFICE:1972 484-483/ 116 1-3